SYNTHESES AND REARRANGEMENT REACTIONS OF SOME TERTIARY PHOSPHINE COMPLEXES OF RUTHENIUM

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PhD THESIS

UNIVERSITY OF EDINBURGH

1977

To my mother and my aunt.

ACKNOWLEDGEMENTS

I am deeply indebted to Dr. T.A. Stephenson for his unfailing help, encouragement and enthusiasm throughout the course of this work. I would also like to thank Professor E.A.V. Ebsworth, Dr. S. Cradock and my fellow students for many helpful discussions. I am very grateful to Dr. E.S. Switkes for allowing the reproduction of some of her results which overlapped with this work. My thanks are also due to Mrs. D.E. Roberts for typing this thesis, Mr. J.R.A. Miller for recording ^{1}H nmr spectra, Dr. A.S.F. Boyd for measuring ^{31}P nmr spectra and finally to the Science Research Council for financial support.

ABSTRACT

Chapter 1 The basic principles of nmr are described and some of the techniques and applications of ^{31}P nmr are given. ^{31}P chemical shifts for monotertiaryphosphine co-ordination compounds are tabulated.

Chapter 2 After a brief survey of monotertiaryphosphine complexes of ruthenium, the preparation of the compounds RuX_2L_3(L = $PEtPh_2$), RuX_2L_4(L = $PMePh_2$, PMe_2Ph) and $Ru_2X_4L_5$(L = $PClPh_2$, PEt_2Ph) by the reaction of tertiary phosphine with $RuX_2(PPh_3)_{3 \text{ or } 4}$ (X = Cl,Br) in hexane or light petroleum is reported. The structures and rearrangement reactions of these compounds in polar and non-polar media are examined chiefly by means of ^{31}P nmr spectroscopy and possible mechanisms for the rearrangements are discussed. In non-polar solvents $RuCl_2(PPh_3)_3$ loses a PPh_3 group whereas in highly polar solvents dissociation of a chloride ligand occurs. $RuCl_2(PEtPh_2)_3$ rearranges to $[Ru_2Cl_3(PEtPh_2)_6]Cl$ in polar solvents and to $Ru_2Cl_4(PEtPh_2)_5$ in non-polar solvents. $RuCl_2(PMePh_2)_4$ rearranges in solution to form $Ru_2Cl_4(PMePh_2)_5$ and $[Ru_2Cl_3(PMePh_2)_6]Cl$ cis-$RuCl_2(PMe_2Ph)_4$ readily rearranges to $[Ru_2Cl_3(PMe_2Ph)_6]Cl$.

Chapter 3 The preparations of the complexes $Ru_2Cl_4(CS)_2(PPh_3)_4$ and $Ru_2Cl_4CS(PPh_3)_4$ are given. A mechanism involving the 5 co-ordinate intermediate "$RuCl_2CS(PPh_3)_2$" is invoked to explain their formation and also that of $Ru_2Cl_4(CS)_2(PPh_3)_3$ from $Ru_2Cl_4(CS)_2(PPh_3)_4$. $Ru_2Cl_5CS(PPh_3)_3$ is formed from $Ru_2Cl_4CS(PPh_3)_4$ by intermolecular displacement of PPh_3 by Cl.

Chapter 4 $RuCl_2CO(PPh_3)_2$dmf dissolves in non polar solvents to form the five co-ordinate "$RuCl_2CO(PPh_3)_2$". This is used to verify the rearrangement mechanism proposed in Chapter 3 by

synthesising the corresponding carbonyl complexes $Ru_2Cl_4(CO)_2(PPh_3)_3$ and $Ru_2Cl_4CO(PPh_3)_4$. In polar solvents $[Ru_2Cl_3(CO)_2(PPh_3)_4]^+$ is formed. ^{31}P nmr is used to study these reactions. Equimolar quantities of $RuCl_2CO(PPh_3)_2dmf$ and $RuBr_2(PPh_3)_3$ (or $RuBr_2CO(PPh_3)_2dmf$ and $RuCl_2(PPh_3)_3$) react to form $Ru_2Br_2Cl_2CO(PPh_3)_4$.

Chapter 5 $RuCl_2CO(PEtPh_2)_3dmf$ is prepared as the corresponding PPh_3 complex. It rearranges in a similar manner and although the products may not be obtained in pure form they may be identified by ^{31}P nmr. $[Ru_2Cl_3(CO)_2(PEtPh_2)_4]^+$ forms more readily than its PPh_3 analogue. $RuCl_2CO(PEtPh_2)_3$ is also formed as a major product in these reactions.

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CHAPTER ONE

BASIC PRINCIPLES OF NMR SPECTROSCOPY AND SOME USES OF ^{31}P NMR IN THE STUDY OF METAL CO-ORDINATION COMPLEXES

1.1 Introduction

The first experiments involving Nuclear Magnetic Resonance (n.m.r.) spectroscopy were carried out in 1945. Since then the subject has developed and expanded rapidly (particularly so in recent years), such that its importance has grown to equal, if not to surpass that of the other spectroscopic techniques.

N.m.r. makes use of the intrinsic angular momentum or spin possessed by the nuclei of certain isotopes and the magnetic energy of these nuclei when placed in a magnetic field.

The usefulness of a nucleus depends upon its natural abundance, sensitivity and of course upon the chemical importance of the atom it characterises. Most work has concerned itself with nuclei for which the nuclear spin quantum number (I) has the value $\frac{1}{2}$[†], of which the hydrogen nucleus (^{1}H) is the most important. However, recently an increasing amount of research has concerned itself with other less sensitive nuclei for which I also has the value $\frac{1}{2}$, namely phosphorus (^{31}P), fluorine (^{19}F) and carbon (^{13}C).

1.2 Basic Theory[††]

When a magnetic nucleus of spin $\frac{1}{2}$ such as ^{1}H, ^{13}C, ^{31}P, is held in a strong homogeneous magnetic field, it tends to align itself in one

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[†] Nuclei for which I is greater than $\frac{1}{2}$ possess an electrical quadrupole moment which often leads to broadening of the n.m.r. spectrum

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[††] from references (1-10)

of two theoretically permissable directions with respect to that field. These directions correspond to the nuclear spin vector being either parallel (lined up with) or antiparallel (lined up against) to the polarising field, and represent slightly different nuclear energy levels: i.e. states with spin quantum numbers (I) equal to $-\frac{1}{2}$ or $+\frac{1}{2}$ respectively. A decrease in energy corresponds to aligning the vector with the magnetic field, and conversely, aligning the vector in opposition to the field corresponds to an increase in energy.

The energy difference between these states ΔE, is proportional to the strength of the applied field B and the magnetogyric ratio γ (which is the ratio of the magnetic moment and the angular momentum of the particular nucleus and which has a characteristic value for each magnetically active nucleus (^{1}H, ^{31}P etc.)). The magnitude of the energy difference may be obtained from equation (1).

$$\Delta E = \frac{h\gamma B}{2\pi} \qquad (1)$$

(h is Planck's constant)

Transitions between the two energy levels can be produced by supplying the appropriate amount of energy in the form of electromagnetic radiation (for n.m.r. the radiation is in the radiofrequency part of the electromagnetic spectrum):-

$$\Delta E = h\nu \qquad (2)$$

(ν is the frequency of the radiation)

$$\nu = \frac{\gamma B}{2\pi} \qquad (3)$$

This condition may be satisfied by varying either ν (the radio-frequency) or B (the magnetic field). It is more usual now to use a frequency (varying ν) although previously field sweep (varying B) was used extensively in the study of ^{31}P and ^{19}F nuclei.

The low frequency of nuclear magnetic resonance absorption indicates that the energy separation of the spin states is quite small. The nuclei in each of the states are in equilibrium and the numbers of nuclei in the different spin states does not differ greatly. If there exists a Boltzman distribution between the spin states, then it would be expected that the population of the lower energy state would be the greater. Because the lower energy state has a slightly higher proportion of nuclei, there will result a net absorption of energy when the sample is perturbed (normally by applying a sinusoidally oscillating magnetic field at right angles to the magnetic field B).

This perturbation is detected electronically by a coil wound around the sample and the resulting signal is amplified and displayed on an oscilloscope or is recorded.

As the numbers of nuclei in each state are very nearly equal, then the population of each of the two energy levels can very quickly become equalised by the application of the external energy source i.e. the sample is saturated.

The lifetime of a nucleus in any particular orientation is limited however as a result of relaxation pathways arising chiefly from the fluctuating field experienced by the nucleus, due to the magnetic moments of the other nuclei in other molecules as they execute Brownian motion. If there are paramagnetic species present (usually transition metal ions) relaxation rates are increased due to the larger magnetic moment of an electron compared with a nucleus. Relaxation times therefore may be reduced by adding such species to the sample;

$Fe(acac)_3$ and $Cr(acac)_3$ (acac = acetylacetonate) are usually used. The times taken for the system to relax depends upon the particular environment of each nucleus.

1.3 The Magnetic Field at the Nucleus

So far it has been shown that a single isotope gives rise to a single nuclear magnetic resonance in an applied field. This in itself would be of little interest except for the fact that the magnetic field at the nucleus is never equal to the applied field, but depends in many ways upon the structure of the molecule in which the atom carrying the nucleus resides.

When an atom or molecule is placed in a magnetic field, as a result of the motion of both bonding and non bonding electrons, a secondary magnetic field is set up thereby partially shielding (or screening) the nucleus from the influence of the applied magnetic field. The field experienced by the nucleus is:-

$$B = B_o(1 - \sigma) \qquad (4)$$

B_o is the external field strength

σ is known as the shielding constant

Thus if the observed nuclei are present in chemically different environments, and since the shielding effect is caused by electronic environment, then values of σ will vary with the position of the nucleus in the molecule. The resonance condition (equation 3) must be altered to take account of this effect and becomes:-

$$\nu = \frac{\gamma B_o(1 - \sigma)}{2\pi} \qquad (5)$$

Therefore variations in absorption line positions are observed. These differences in position for nuclei of the same kind which are in

different molecular environments are called chemical shifts (designated δ). The numerical values of these shifts are quoted in terms of parts per million (ppm) with respect to an external standard. δ is related to the shielding constants by the equation:-

$$\delta = 10^6(\sigma \text{ ref} - \sigma \text{ sample}) \qquad (6)$$

A high frequency shift implies a decrease in σ i.e. a deshielding.

The bases for chemical shifts can be accounted for theoretically in principle, but a priori calculations in general cannot at present provide exact values for these quantities.[8] Predictions of chemical shifts for nuclei in particular environments must be made on the basis of empirical correlations between observed shifts and chemical structure. Tables have been produced to show a correlation between chemical shift and functional groups.[8]

The Ramsey formulation,[12,13] is probably the most useful in furnishing a framework for discussing chemical shifts and the factors which influence them. In general there are five terms which contribute to the shielding constant(σ)

(i) the diamagnetic contribution from the atom in question, σd

(ii) the paramagnetic contribution from the atom in question, σp

(iii) the effect of the neighbouring atoms

(iv) interatomic currents

(v) the effect of external electric fields

The diamagnetic screening contribution is related to the mechanism which gives rise to the diamagnetism of materials. This effect is a maximum for a free atom where electrons can circulate freely, but in a molecule the free circulation around an individual nucleus is hindered by the bonding and by the presence of other positive centres, so that the screening is reduced and the nuclear frequency increased.

Since this mechanism reduces the diamagnetic screening it is known as the paramagnetic effect. This does not imply the presence of unpaired electrons.

Since the magnitude of σd depends upon the density of circulating electrons, it is common to find in the literature discussion of the effect of inductive electron drifts on the screening of nuclei-particularly in organic chemistry where good correlations have been found between screening constants and substituent electronegativity. However, it is currently believed that the contribution of inductive effects is small at least for σ bonded systems.(7)

The paramagnetic contribution (σp), which is sometimes referred to as the temperature independent paramagnetic term, is opposite in sign to σd. This term which is zero for ions with spherically symmetrical s states corrects for the fact that the electrons in a molecule are not generally disposed with spherical symmetry about the nucleus in question.(8)

σp is determined by several factors:-

(a) The inverse of the energy separations between the ground and excited electronic states of the molecule. This means that correlations are found between shielding constants and the frequency of absorption lines in the visible and ultra-violet spectra.

(b) The relative electron densities in the various p orbitals involved in bonding i.e. upon the degree of asymmetry in electron distribution near the nucleus.

(c) The value of $\langle {}^{1}/_{r}{}^{3} \rangle$, the average inverse cube distance from the nucleus to the orbitals concerned.

In the case of hydrogen, for which there are few electrons to contribute to the screening and for which ΔE is large, σd and σp are both small and only a small change in σ is observed among its compounds.

As z (the atomic number) increases, ΔE decreases, there are more electrons present so σp and σd both increase: σp increases disproportionately and dominates the screening. The observable changes in screening do not increase continuously with atomic number but exhibit a periodicity, being a minimum at the top and a maximum at the bottom of a group (a consequence of the $^1/_r 3$ term).[7,8]

The changes observed in screening among the compounds of one element depend primarily upon factors (i) and (ii) above; which means that they are determined by such factors as bond angles and bond order.[7]

While variation in electron density around the nucleus in question is probably the most important factor influencing its chemical shift, many exceptions are found in correlations between δ and electron density. To account for these cases, it is necessary to consider the induced magnetic fields which have their origins in atoms or functional groups near the atom in question.

The magnetic fields at the nucleus due to all other magnetic dipoles will only average to zero, in the spinning liquid sample, if the magnet has the same dipole strength whatever the orientation of the molecule relative to the field. If the source of magnetism is anisotropic and the dipole strength varies with orientation in the applied field then a finite magnetic field appears at the nucleus. Such anisotropic screening is observed in nitriles, acetylenes, aromatic compounds ("ring currents") etc.[7,8]

Molecules which contain electric dipoles or point charges possess an electric field whose direction is fixed relative to the rest of the molecule. Such electric fields can perturb the molecular orbitals by causing electron drifts at the nuclei in the bond directions and by

altering the electronic symmetry. Screening due to such electric fields is given the symbol σe. The effect of the electric field is intramolecular and is attenuated with increasing distance.[7]

External electric fields arise from the effect of the solvent medium on nuclear shielding. This effect has been expressed as the sum of five terms[8]:-

$$\sigma\ (\text{solvent}) = \sigma_B + \sigma_W + \sigma_A + \sigma_E + \sigma_H \qquad (7)$$

(i) σ_B is the contribution of the bulk magnetic susceptibility of the medium.

(ii) σ_W arises from the effect of the weak Van der Waals forces between solute and solvent molecules. Such effects can distort and/or change the symmetry of the electronic environment of a given nucleus. σ_W is negative (causes a shift to high frequency).

(iii) σ_A refers to the magnetic anisotropy in the solvent molecules and arises from the non-zero orientational averaging of solvent with respect to solute

(iv) σ_E arises from the effect of an electric field on the nuclear shielding.

(v) σ_H refers to specific solute-solvent interactions, the most important of which is hydrogen bonding.

An investigation of the variation in chemical shift with solvent has been carried out for the complexes trans-Pt H $L(PEt_3)_2$ ($L=NO_3, NO_2$, Cl, SCN, Br, CN, I, NCS).[14] Results show that for ^1H the variation in solvent shifts are in the order:-

$$\delta(C_6H_6) < \delta(C_6H_{12}) < \delta((CH_3)_2CO) < \delta(CHCl_3)$$

However this order is different for the other magnetic nuclei

in the same molecule; in this case ^{31}P and ^{195}Pt. For platinum the solvent shifts are large (a difference of 16ppm being observed between $\delta(CH\ Cl_3)$ and $\delta(C_6H_{12})$) and are in the order:

$$\delta(CH\ Cl_3) < \delta(C_6H_6) < \delta((CH_3)_2CO) < \delta(C_6H_{12})$$

Whilst the solvent shifts for δP are in the order:

$$\delta(C_6H_{12}) \sim \delta((CH_3)_2CO) \sim \delta(C_6H_6) < \delta(CHCl_3)$$

All of these factors which influence the screening constant, have been summarised[15] in terms of three contributions:-

$$\sigma = \sigma d + \sigma p + \sigma \text{ (other atoms)} \qquad (8)$$

1.4 Spin-Spin Coupling

In addition to differences in shielding between nuclei, interaction may also occur between the magnetically active nuclei in the molecule producing fine structure on the different resonance lines.

Theoretical considerations indicate that the interaction occurs via the bonding electrons. The contact between one nucleus and its s electrons perturbs the electronic orbitals around the atom and so carries information about the nuclear energy to other nearby nuclei in the molecule and so perturbs their nuclear frequency. The interaction or "coupling" gives rise to a multiplet of peaks.†

The magnitude of this interaction which is independent of magnetic field strength is measured in terms of the coupling constant (J). Values of J are quoted in Hertz (Hz). The magnitude of the effect for a particular pair of nuclei depends on the following factors:

(i) The nature of the bonding system; i.e. upon the number and bond order of the bonds intervening between the nuclei and upon the angles

†For a general theory of analysis of coupling constants see refs. 16, 17, 18, 20

between the bonds. The interaction is not usually observed over more than five or six bonds and tends to be attenuated as the number of bonds increases, although many cases are known where coupling over two bonds is less than coupling over three bonds.[7]

(ii) The magnetic moments of the two nuclei, and is directly proportional to the product $\gamma_A \gamma_B$ where γ_A and γ_B are the magnetogyric ratios of the interacting nuclei.

(iii) The valence s electron density at the nucleus and therefore upon the s character of the bonding orbitals. This factor also means that the interaction increases periodically as the atomic number of either or both nuclei is increased, in the same way as does the chemical shift range, eg. for B_2H_6 (Small z) $^1J_{HB}$ ca 43 to 125 Hz[19] and for $HgBr_2(PBu_3)_2$ (z large) $^1J_{HgP}$ is 4777 Hz[20].

In the simple case (first order coupling) the splitting of the resonances is small compared to the chemical shift difference between them. In this case the number of lines into which each resonance is split is given by the formula:

$$\text{no. of lines} = 2nI + 1 \qquad (9)$$

where there are n other nuclei of spin I.

The relative intensities of the resonances within the multiplet are given by the coefficients of x in the expansion of $(1 + x)^n$. In such systems when $J << \delta$, then letters far apart in the alphabet are used to describe the different nuclei eg. AX, AX_2.

However when the size of the coupling constants between non equivalent atoms in the same molecule are of a magnitude which is comparable to or larger than the chemical shift difference between them, then the effects due to spin coupling and chemical shift have similar energy and become intermingled, leading to alterations in the relative

line intensities and in line positions. Under these circumstances these simple rules may no longer be applied. These spectra are said to become second order and to signify this the spins are labelled with letters close together in the alphabet eg. AB, ABC. Mixed systems are also possible eg. ABX.

The perturbation of the spectra from first order appearance is a function of the ratio:

$$\frac{\nu o\ \delta}{J} \qquad (10)$$

νo - spectrometer operating frequency

δ - chemical shift

J - coupling constant

The determination of chemical shifts and coupling constants for these second order spectra may be obtained by direct quantum mechanical calculations.[1,3] These calculations are usually lengthy and are best done by computer. However, for certain of the more simple types of second order spectrum eg. AB, AB_2, the application of simple rules and formulae (see appendices I & II) enable the calculation of δ and J.

Line positions, coupling constants and signal intensities are all important features of spin-spin multiplets, providing information on the number of spin-coupled nuclei, their equivalence and the relative position of these atoms in the structure.

1.5 Applications

The chemical shift and the coupling constant have served to provide valuable information with regard to structure or conformation determination, elucidation of reaction mechanism and kinetics, as well as insight into the nature of the bonding present in compounds and complexes. Considerable

data are available upon the magnitudes of interproton spin coupling constants from the mass of data accumulated for organic compounds. More recently, with rapid advances in instrumentation, the availabe information on the chemical shifts and coupling constants of other nuclei such as ^{11}B, ^{13}C, ^{19}F, ^{31}P has also increased.

A vast number of transition metal complexes is now known in which the central metal atom is bonded to several monodentate (eg. carbonyl, hydride, phosphine, halide) or bidentate (eg. 2,2'-bipyridyl, dithioacids) ligands. The stereochemistry of such complexes offers considerable variation and nmr has been found invaluable in deciding just how the ligands are arranged around the metal atom.

The vast majority of the research which has employed nmr spectroscopy has concerned itself with the hydrogen nucleus (^{1}H). However the range of chemical shifts observed for protons (ca. 20ppm) is small and, with few exceptions, metal coordination compounds of the type $MX_2(PR_3)_4$ (X = halide, hydride etc; R = alkyl and/or aryl) involve complex homonuclear and heteronuclear coupling: hence the ^{1}H nmr spectra of these complexes often provide little useful information (see later chapters).

The phosphorus nucleus (^{31}P) however, displays a much wider range of chemical shifts then does the proton. Furthermore it is possible by arranging to irradiate the sample at the resonant frequencies of the protons, to remove the coupling (decouple) between the ^{1}H and ^{31}P nuclei and hence simplify the spectrum. ^{31}P nmr spectroscopy has therefore been an invaluable technique in the study of transition metal coordination compounds with phosphorus containing ligands.[10, 16, 21]

1.6 Some Aspects of ^{31}P nmr Spectroscopy

Although the isotope ^{31}P has 100% abundance, its inherent sensitivity to nmr detection is only 6.4% of that of the proton. Until recently it has been common to use large non-spinning samples with attendant loss of resolution, although with more modern equipment better signal to noise ratios have been achieved. With large chemical shift differences and large coupling constants common for phosphorus compounds, broad lines were fairly acceptable.

The most commonly used reference compound for phosphorus nmr spectroscopy is 85% phosphoric acid which gives a single rather broad line: this is always used as an external reference. However other compounds have been used chiefly P_4O_6, $P(OPh)_3$, $PO(OMe)_3$ PEt_3, $P(OMe)_3$ As mentioned in section 1.3, solvents can have a moderate effect upon ^{31}P chemical shifts and it is seldom worthwhile determining these to closer than ±0.1ppm.

The poor sensitivity of the ^{31}P nucleus is unfortunate especially where large quantities of the sample are not available or in cases where the amount of phosphorus in the molecule is small (e.g. $Cr(CO)_5PPh_3$, which contains only 7% phosphorus by weight). In these situations random electronic noise often obscures the resonances. As a result there has been considerable preoccupation with ways of increasing the signal to noise ratio of nmr spectrometers.

In this connection, use can be made of electronic filtration or CAT-ing (Computer Averaging of Transients). These processes can, unfortunately be extremely time consuming, a difficulty which may be overcome by the use of a recent development, that holds great promise for signal enhancement, namely the technique of Fourier Transform Spectroscopy.

In this technique,[8,11] instead of using a steady R.F. (radio-frequency) field the sample is subjected to a very short (about 100μ-sec duration) intense pulse radiofrequency power, close to the ^{31}P resonant frequency. As a result the entire spin system will be seriously perturbed and the resultant exponential decay pattern as it regains equilibrium will contain all the information present in a slow passage spectrum. Since the spectrum of the sample generally consists of many lines, not just one, this pattern is not a simple free induction decay but is modulated by interference effects. A single transient response can be collected in a very short time; usually between 0.4 and 10 secs (the longer the time the better the resolution).

It can be shown that the response pattern is just the Fourier transform of the spectrum and the "normal" spectrum can be extracted by taking the inverse Fourier transform, a task easily done by computer. The advantage of this technique is that the pulse can be repeated and a large number of decay patterns added in a small storage computer before the Fourier transform is performed to produce a spectrum of high signal to noise ratio. Since noise is random it can be shown that the noise after N seconds has only increased by $\sqrt{N}$ so that there is a signal-to-noise improvement of $\sqrt{N}$ (in practice the improvement is somewhat less than this).

At the same time as the spectrum is being recorded the other magnetic nuclei coupled to phosphorus (most commonly ^{1}H) may be decoupled by irradiation. Such saturation of the resonances of the protons can affect the relaxation of the phosphorus nuclei, thereby causing intensity changes in the nmr spectrum.

This phenomenon (The Nuclear Overhauser Effect) occurs when the nuclei in question are physically close, although there need not

necessarily be any spin coupling between them. It is then found that the relaxation of the observed nuclei may depend mainly upon spin exchange with the irradiated one, so that saturation of the latter can give an intensity enhancement in the former.[11] In ^{13}C spectra in which the protons are decoupled, the Overhauser effect leads to an increase in intensity of those carbons carrying hydrogen of about three times.[7] A very recent study has shown that saturation of all of the protons in phosphorus compounds can lead to an increase in the intensity of the phosphorus resonances i.e. a Nuclear Overhauser Effect enhancement of up to 124%.[22] Despite the welcome intensity increases which the Overhauser effect brings, it means that the intensity data useful for counting the ratios of nuclei present, are no longer reliable.

It has been shown in section 1.3 that chemical shifts represent a summation of environmental effects on the magnetic properties of the atom. Products of many reactions involving phosphorus-containing ligands have large ^{31}P environmental differences, so that the nmr patterns of these may be readily interpreted. Other reaction products do not exhibit such gross differences so that the unambiguous assignment of peaks solely on the basis of chemical shifts may become considerably more difficult. In cases where the possible products of a reaction cannot be reduced to a choice between two or three alternative structures, then chemical shift data may offer little help in the assignment of peaks. Here a careful study of any fine structure due to spin-spin interactions can be of considerable aid in product identification.

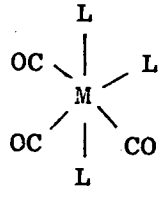
1.7 Some Applications of ^{31}P nmr to Metal Coordination Complexes

It has been shown for organophosphorus compounds that a linear relationship exists between ^{31}P chemical shifts and Hammett constants.[23] In addition, Grim et al.[24,25] have shown that the values of ^{31}P chemical shifts for tertiary phosphines may be calculated by summation of "contributions" from the substituent alkyl and aryl groups attached to the phosphorus atom.

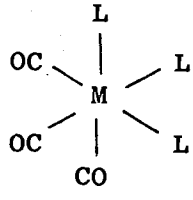
However, this cannot be extended to tertiary phosphine† metal[20] coordination compounds as a whole, where no general theory exists which has proved satisfactory for the calculation of ^{31}P chemical shifts.

Despite the lack of a general theory ^{31}P data have nonetheless proved to be useful. This area has been the subject of extensive investigation and review.[10,16,21,26,27,28,29] Some important uses of ^{31}P nmr as applied to metal complexes are summarised below and some selected examples quoted. Tables 1-17 contain phosphorus chemical shift data for monotertiary phosphine complexes.

The complexes mer-(meridional) and fac-(facial) $Cr(CO)_3(PMe_3)_3$ (I and II respectively) are easily distinguised by ^{31}P nmr; the spectrum of I comprising a doublet (21.4ppm)* and triplet (10.3ppm)



I



II

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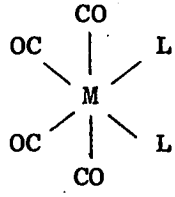
†The term tertiary phosphine here refers to tri-alkyl, dialkylaryl, alkyldiaryl and tri-aryl monotertiary phosphines.

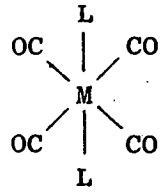
*Chemical shifts are quoted with respect to 85% H_3PO_4 and are positive to high frequency as suggested by I.U.P.A.C.[30]

pattern, and that of II a singlet (3.8ppm).[31]

However with the complexes cis - and trans - $Cr(CO)_4(PMe_3)_2$ (III and IV) the task is not so easily performed as both complexes give rise



III



IV

to a single phosphorus resonance at 6.5ppm and 21ppm respectively.[31,32] Indeed from the observations made by Shaw et al.,[33-36] that ^{31}P - ^{31}P couplings of trans - orientated ^{31}P nuclei are large and are characterised by apparent triplets in the ^{1}H spectrum, while cis - couplings are small giving an unperturbed doublet, it would be expected that these two isomers could be distinguished by ^{1}H nmr. However caution must be exercised in applying this rule as many cis - complexes have appreciable P-P coupling. This is especially true of complexes of manganese[37] and of chromium where $^{2}J_{PMP}$ is greater in some cis - complexes than in the trans - complexes. In the case of III and IV ($L = PMe_3$) above, $^{2}J_{PMP}$ cis - is -36 Hz and $^{2}J_{PMP}$ trans - is -28.5 Hz[32] contrary to the observations of Shaw et al.

Obviously in the case of $Cr(CO)_4(PMe_3)_2$ the two isomers are readily distinguished by an examination of the carbonyl region of the infra-red spectrum of each complex. However, often it is also possible to distinguish between isomers on the basis of the differences in chemical shift exhibited by the two resonances.

In the complex mer - $Cr(CO)_3(PMe_3)_3$(I) the resonance of the phosphorus nucleus trans - to a carbonyl group occurs to low frequency

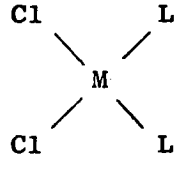
of that due to the mutually trans - phosphines.[31] Examination of the other data for chromium complexes (table 1) shows that in general:-

$$\delta \text{ (P trans - to CO)} < \delta \text{ (P trans - to P)}$$

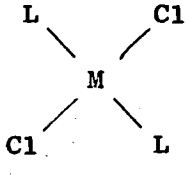
Similar observations may be made for molybdenum (table 5) and tungsten (table 12). Hence it would be possible to predict that the phosphorus resonance for cis - $Cr(CO)_4(PMe_3)_2$ would come to low frequency of that of the trans - isomer.

This phenomenon observed by Grim et al.[38] for the disubstituted derivatives of $P(Ph_3)_{3-n}R_n$ phosphines has been shown to be applicable to higher degrees of substitution.[31] Of course the ^{31}P chemical shift is not influenced solely by the ligand occupying the trans - position, and the observation cannot be considered as a firm rule. However, it does provide a qualitative guide as to the nature of the complex.

Unfortunately the observation made for one metal cannot be generalised to cover other metals or other ligands. Thus whereas the ^{31}P chemical shift of the cis - isomer (V) of $PtCl_2L_2$ for a particular tertiary phosphine is always to low frequency of that of the trans - complex VI, for the corresponding palladium complexes the opposite appears to be true (see tables 8 and 16).



V



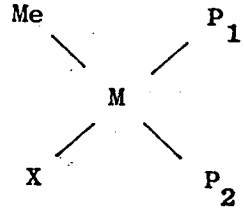
VI

As mentioned above, in addition to ^{31}P chemical shifts, use can also be made of the phosphorus - phosphorus coupling constants in the determination of the structure of a coordination complex,[16] chiefly

by means of the observation,[16,37] that $^{2}J_{PMP}$ is generally greater in a complex in which the phosphorus nuclei are mutually trans - than when they are mutually cis -.

However, in addition many transition metals have magnetically active nuclei eg. ^{103}Rh, ^{183}W, ^{195}Pt have $I = \frac{1}{2}$, and coupling can often be observed between the phosphorus nucleus in the donor ligand and the nucleus of the acceptor atom.

It has been found for certain metals that the values of the coupling constants are much more sensitive to the nature of the trans - ligand than they are to the nature of the cis - ligands.[16] Thus it has been shown for platinum and rhodium that when a phosphine ligand is trans - to a chloride ligand that the phosphorus to metal coupling constant is greater than in the case when it is trans - to another phosphine ligand[16, 39-41], and that in both cases it is greater than when the phosphine is trans - to a methyl or phenyl group: eg. in the complexes cis - and trans - $PtMeCl(PEt_3)_2$ - for the cis - complex (VII; X = Cl) the phosphorus nucleus trans - to Cl (P_1),



VII

$^{1}J_{PtP}$ is 4179 Hz and for that trans - to Me (P_2), $^{1}J_{PtP}$ is 1719 Hz. In the all trans - complex $^{1}J_{PtP}$ is 2821 Hz.[16] In addition it would appear that for tungsten that the value of $^{1}J_{WP}$ is greater when the phosphine ligands are mutually trans - rather than when a carbonyl group occupies the trans - site. Thus in cis - $W(CO)_4(PBu_3)_2$ (III) $^{1}J_{WP}$ is 225 Hz and in the trans - isomer (IV) $^{1}J_{WP}$ is 265 Hz.[42]

Information as to stereochemistry can therefore often be obtained by comparison of the spin coupling constant values of the unknown complex with those for a complex in which the relative positions of the phosphine ligand is known.

Recent research [43-46] has shown that a good linear correlation exists between the chemical shift of a free tertiary phosphine (δp) and the change in chemical shift of that phosphine on coordination (Δ)

$$\Delta = A\delta p + B \qquad (11)$$

The values of A and B are constant for a particular complex (eg. for $RhClCOL_2$ A = -0.335 ± 0.026; B = 35.88 ± 0.69) but vary between complexes. The relationship expressed in equation 11, which had been noted previously for fluorophosphine complexes,[47] has been shown to hold for a wide range of complexes of the metals Cr, Ni, Mo, Ru, Rh, Pd, W, Ir, Pt.[45]

Thus, it is possible to predict the coordination chemical shift (Δ) of a tertiary phosphine ligand in one of these complexes provided that the chemical shift of the uncomplexed phosphine is known.

An exception is to be found in methyldiphenylphosphine whose Δ values can not usually be calculated by equation (11). Molecular models have shown that the $PMePh_2$ complexes are extremely crowded and because of the asymmetry of the ligand they probably have conformers of very unequal probabilities giving rise to the ambiguities.[46]

So far only the way in which ^{31}P nmr may be used to determine the stereochemistry of a single coordination complex has been considered. However, very often chemical reactions do not give rise to only one product. It is sometimes possible to separate the mixtures obtained in these reactions by differences in solubility or by chromatographic methods. Should such techniques prove impracticable then the nature

of the reaction products could be determined by a careful analysis of the ^{31}P nmr spectrum.

In addition to examining the mixtures of reaction products ^{31}P nmr has also been used to examine the species present during the course of chemical reaction. Very recently this technique has been applied to the equilibrium:

$$[HML_3]^+ + L \rightleftharpoons [HML_4]^+ \qquad (12)$$

$$M = Ni, Pd, Pt; \quad L = PEt_3$$

By recording spectra at various temperatures and utilising a computer line shape programme, it was possible to extract detailed mechanistic information (M = Pd) concerning the mode of attack of the ligand and the site occupied by the ligand in the five coordinate species, as well as thermodynamic parameters.[48,49] Much of the information obtained by this means would have been unavailable using any other approach.

^{31}P nmr spectroscopy has also been used to examine the nature of certain complexes in solution. A recent investigation of the complexes PdL_n (n = 2,3,4, L = various tertiary phosphines)[50] in solution and their exchange reactions with tertiary phosphines has used this method.

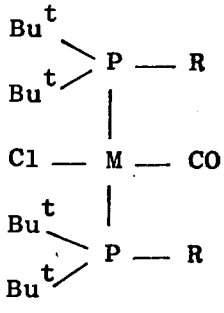
By arranging the system such that tertiary phosphine exchange was slow (usually by cooling the system) it was possible to identify the complexes present in solution and by a variable temperature investigation of PdL_n with an excess of tertiary phosphine, thermodynamic parameters were obtained (using a line shape calculation program) for the exchange of free and complexed phosphine.

By varying the temperature at which the ^{31}P nmr spectrum is recorded, it is possible to obtain further information about the behaviour in

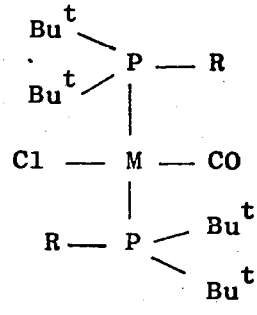
solution of the complex under scrutiny. For many compounds the rate of intra- or inter-molecular exchange is fast at ambient temperatures. In this case it is the exchange of free and bound phosphine which is being investigated. By cooling the solution the rate of exchange can be reduced until it is sufficiently slow to make possible the observation of the "frozen-out" structure of the complex. Alternatively when the rate of exchange is slow at room temperature this can be increased by increasing the temperature at which the spectrum is recorded.

When a sample is to be studied at temperatures other than room temperature a solvent must be chosen which when cooling the sample will not freeze before exchange has become sufficiently slow to identify the species present or when heating will not boil before exchange has become rapid.

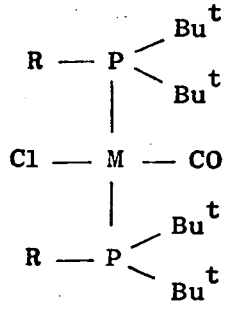
By using ^{31}P nmr it has been possible to show that the complexes trans - $MClCO(PR(t\text{-}Bu)_2)_2$ (M=Rh, Ir; R = Me, Et, n-Pr) exists in solution as a mixture of three conformers[51] (VIII, IX, X)



VIII



IX



X

The conformers VIII and X give rise to a singlet (M = Ir) or a doublet (M = Rh) resonance. The chemical shift difference between these resonances can be as small as 5ppm (M = Rh; R = Et) and as great as 16ppm (M = Rh; R = Me). The third conformer IX gives rise to an AB spectrum (M = Ir) or an ABX spectrum (M = Rh).

It is obvious that ^{31}P nmr provides a hitherto unavailable means of characterisation and detailed investigation of the solution chemistry of transition metal co-ordination compounds containing phosphorus ligands. As has been seen, the identity of an unknown compound can be hypothesised from agreement between its measured chemical shift and the previously measured chemical shift of the same compound or a related compound. (Chemical shift data for some tertiary phosphine complexes have been tabulated (tables 1-17) to assist in any such analysis). However since this is a necessary but not sufficient condition, additional supporting evidence is desirable to confirm the analysis. This may be obtained from the spin-spin coupling constants or by auxiliary analytical techniques.

TABLES OF ^{31}P CHEMICAL SHIFTS

OF METAL CO-ORDINATION COMPOUNDS

Only the metal complexes formed with monotertiaryphosphines containing alkyl and/or aryl substituents are quoted in these tables, but where another phosphorus nucleus exists in the molecule its chemical shift is also given, where available. Where a complex contains more than one tertiary phosphine, the complex appears under each of the phosphines in the table. In all cases chemical shifts are quoted in parts per million to high frequency of 85% H_3PO_4, The numbers in parenthesis after the chemical shift values refer to the approximate relative intensities of the two signals.

Table 1 ^{31}P Chemical Shifts of Monotertiaryphosphine Complexes of CHROMIUM

Compound	L	δP(ppm)	Ref.
cis - $Cr(CO)_2L_4$	PMe_3	16.5(trans-) 5.4(cis-)	31
fac - $Cr(CO)_3L_3$	"	3.8	31
mer - $Cr(CO)_3L_3$	"	21.4(2) 10.3(1)	31
cis - $Cr(CO)_4L_2$	"	6.7,6.3	31,32
trans - $Cr(CO)_4L_2$	"	20.7,21.0	31,32
$Cr(CO)_5L$	"	6.5	31
trans - $Cr(CO)_4L_2$	PBu_3	44.2	38
$Cr(CO)_5L$	"	30.2	52
trans - $Cr(CO)_4(P^1Ph_3)L$	"	43.3 (P^1)74.1	53
trans - $Cr(CO)_4(P^1(OPh)_3)L$	"	38.2 (P^1)185.1	53
cis - $Cr(CO)_4L_2$	PBu_2Ph	32.4	38
trans - $Cr(CO)_4L_2$	"	50.4	38
$Cr(CO)_5L$	"	35.3	52
$Cr(CO)_5L$	$PMePh_2$	35.0	52
$Cr(CO)_5L$	$PEtPh_2$	48.3	52
$Cr(CO)_5L$	P(iso-Pr)Ph_2	59.9	52
cis - $Cr(CO)_4L_2$	$PBuPh_2$	61.5	38
$Cr(CO)_5L$	"	45.1	52
$Cr(CO)_5L$	P(t-Bu)Ph_2	72.7	52
$Cr(CO)_5L$	PPh_3	55.3	52
trans - $Cr(CO)_4(P^1Bu_3)L$	"	74.1 (P^1)43.3	53

Table 1 continued

Compound	L	δP(ppm)	Ref.
$Cr(CO)_2(C_6H_6)L$	"	91.1* 70.9	54
$Cr(CO)_2(C_6H_5.CH_3)L$	"	92.0* 72.0	54
$Cr(CO)_2(C_6H_5.OCH_3)L$	"	92.0* 72.3	54
$Cr(CO)_2(C_6H_5.CO_2CH_3)L$	"	87.0* 79.6	54
$Cr(CO)_2(C_6H_5N(CH_3)_2)L$	"	93.7* 78.1	54
$Cr(CO)_2(p\text{-}C_6H_4(CO_2CH_3)_2)L$	"	82.3* 75.0	54
$Cr(CO)_2(mes)L$	"	92.6* 73.2	54

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*values obtained when spectrum measured in CF_3COOH where protonation of Cr occurs.

Table 2 ^{31}P Chemical Shifts of Monotertiaryphosphine Compleces of IRON

Compound	L	δP(ppm)	Ref.
FeL_4*	PMe_3	P_1 -17.4	55
		P_2 24.1	
		P_3 30.7	
		P_4 38.1	
$Fe(CO)_3L_2$	PPh_3	-9.5	56
$Fe(NO)_2L$	"	50.8	56

*Structure:-

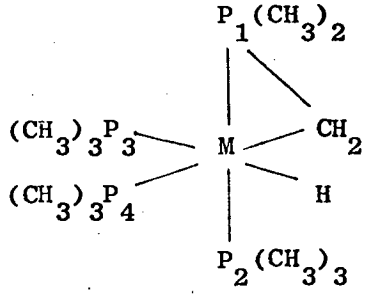


Table 3 ^{31}P Chemical Shifts of Monotertiaryphosphine Complexes of NICKEL

Compound	L	δP(ppm)	Ref.
NiL_4	PMe_3	-22.2	58
$Ni(CO)_2L_3$	"	-18.4	31
$Ni(CO)_2L_2$	"	-18.2	31
$Ni(CO)_3L$	"	-19.9	31
NiL_4	PEt_3	2.4	57
$[HNiL_4]^+$	"	5.0(1) 9.3(3)	49
$[HNiL_3]^+$	"	A_2B pattern A,16.8;B,15.1	59
$Ni(CO)_2L_2$	"	20.2	56
$NiCl_2L_2$	"	15.7,15.0 to 19.3*	60,61
$NiCl_2L_2$	$P(\underline{iso}\text{-}Pr)_3$	72.8 to 44.0*	61
$Ni(CO)_2L_2$	PBu_3	12.1	56
$NiCl_2L_2$	"	-1.5,-1.5, 16 to 3.8*	56,60,61
$Ni(CNS)_2L_2$	"	0	56
$Ni(PhC{\equiv}C)_2L_2$	"	15.1	56
$Ni(CO)_2L_2$	$POct_3$	13.3	56
$Ni(CO)_2L_2$	$P(CH_2CH_2CN)_3$	20.4	56
$Ni(CO)_2L_2$	$P(CH_2CH_2CN)_2Oct$	18.9	56
$Ni(CO)_2L_2$	PEt_2Ph	23.2	56
NiL_4	$PMePh_2$	2.9	57

*measured in a variety of solvents

Table 3 continued

Compound	L	δP(ppm)	Ref.
$NiOTBrL_2$	$PMePh_2$	10.5	62
$NiOTBr(P^1Ph_3)L$	"	9.1 (P^1)26.1	62
$Ni(CO)_2L_2$	$PEtPh_2$	28.7	56
NiL_3	PPh_3	23	63
$Ni(CO)_2L_2$	"	32.6	56
$NiC_2H_4L_2$	"	31	63
$NiOTBrL_2$	"	23.9	62
$NiCpL_2$	"	42.7	64
$NiCp(SnCl_3)L$	"	38.7	64
$NiCp(SnPh_3)L$	"	49.8	64
$NiCp(PbPh_3)L$	"	42.7	64
NiCpClL	"	27.6	64
NiCpBrL	"	32.0	64
NiCpIL	"	41.9	64
NiCpCNL	"	39.7	64
NiCpNCOL	"	27.1	64
$NiCpNO_2L$	"	29.4	64
NiCpNCSL	"	27.9	64
NiCpMeL	"	49.5	64
NiCpEtL	"	49.0	64
NiCp(n-Pr)L	"	49.1	64
NiCp(iso-Pr)L	"	47.6	64
NiCp(n-Bu)L	"	49.1	64
NiCp(iso-Bu)L	"	47.9	64

Table 3 Continued

Compound	L	δP(ppm)	Ref.
NiCp(sec-Bu)L	PPh_3	42.2	64
$NiCp(CH_2CMe_3)L$	"	46.1	64
NiCpPhL	"	41.9	64
$NiCp(CH_2Ph)L$	"	46.7	64
$NiCp(CH_2SiMe_3)L$	"	45.9	64
$NiCp(PhSiMe_3)L$	"	42.3	64
$NiOTBr(P^1(p\text{-}C_6H_4Me)_3)L$	"	23.1 (P^1)22.9	62
$NiOTBr(P^1(p\text{-}C_6H_4OMe)_3)L$	"	22.7 (P^1)22.0	62
$NiOTBr(P^1(p\text{-}C_6H_4F)_3)L$	"	23.0 (P^1)22.7	62
$NiOTBr(P^1(p\text{-}C_6H_4Cl)_3)L$	"	23.3 (P^1)23.2	62
$NiOTBr(P^1(OMe)_3)L$	"	22.7 (P^1)114.7	62
$NiOTBr(P^1(OPh)_3)L$	"	23.0 (P^1)99.4	62
$NiOTBrL_2$	$P(p\text{-}C_6H_4CH_3)_3$	22.1	62
$NiOTBr(P^1Ph_3)L$	"	22.9 (P^1)23.1	62
$NiOTBrL_2$	$P(p\text{-}C_6H_4OMe)_3$	20.5	62
$NiOTBr(P^1Ph_3)L$	"	22.0 (P^1)22.7	62
$NiOTBrL_2$	$P(p\text{-}C_6H_4F)_3$	21.7	62
$NiOTBr(P^1Ph_3)L$	"	22.7 (P^1)23.0	62
$NiOTBrL_2$	$P(p\text{-}C_6H_4Cl)_3$	22.6	62
$NiOTBr(P^1Ph_3)L$	"	23.2 (P^1)23.3	62

Table 4 ^{31}Chemical Shifts of Monotertiaryphosphine Complexes of COPPER

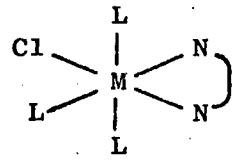
Compound	L	δP(ppm)	Ref.
$[CuL_2I]_4$	PBu_3	-26.0	56
$[CuLI]_4$	"	-34.0 broad	65

Table 5 ^{31}P Chemical Shifts of Monotertiaryphosphine Complexes of MOLYBDENUM

Compound	L	δP(ppm)	Ref.
cis - $Mo(CO)_2L_4$	PMe_3	-18.3(cis-) -8.8(trans-)	31
fac - $Mo(CO)_3L_3$	"	-18.7	31
mer - $Mo(CO)_3L_3$	"	-16.6(1) -6.7(2)	31
cis - $Mo(CO)_4L_2$	"	-14.5,-17.8	31,32
trans - $Mo(CO)_4L_2$	"	-7.0	31,32
$Mo(CO)_5L$	"	-17.3	31
fac - $Mo(CO)_3L_3$	PEt_3	8	31
mer - $Mo(CO)_3L_3$	"	15.7(1) 25.5(2)	31
cis - $Mo(CO)_4L_2$	"	13	31
trans - $Mo(CO)_4L_2$	"	29	31,56
$Mo_2Cl_4L_4$	"	12	65
$Mo(CO)_5L$	"	20	31
$Mo_2Cl_4L_4$	PPr_3	7	65
cis - $Mo(CO)_4L_2$	PBu_3	8.9	38
trans - $Mo(CO)_4L_2$	"	22.4,22.0	38,52
$Mo_2Cl_4L_4$	"	7	65
$Mo(CO)_5L$	"	12.2	52
trans - $Mo(CO)_4(P^1Ph_3)L$	"	22.0 (P^1)50.9	53
trans - $Mo(CO)_4(P(OPh)_3)L$	"	17.2 (P^1)165.0	53
$MoOCl_2L$	PMe_2Ph	3.8(1) 0.8(2)	66

Table 5 continued

Compound	L	δP(ppm)	Ref.
$MoOBr_2L_3$	"	-1.7(1) -3.6(2)	66
$MoOI_2L_3$	"	-13.6(1) -12.0(2)	66
cis - $Mo(CO)_4L_2$	PBu_2Ph	14.5	38
trans - $Mo(CO)_4L_2$	"	28.8	38
$Mo(CO)_5L$	"	17.6	52
cis - $Mo(CO)_4(P^1Ph_3)L$	"	12.1 (P^1)38.3	53
trans - $Mo(CO)_4(P^1Ph_3)L$	"	27.9 (P^1)51.1	53
trans - $Mo(CO)_4(P^1(OPh)_3)L$	"	23.1 (P^1)165.2	53
$Mo(CO)_5L$	$PMePh_2$	15.0	52
$Mo(CO)_5L$	$PEtPh_2$	30.1	52
$Mo(CO)_5L$	$PPrPh_2$	26.5	52
$Mo(CO)_5L$	P(iso-Pr)Ph_2	43.2	52
cis - $Mo(CO)_4L_2$	$PBuPh_2$	25.8	38
trans - $Mo(CO)_4L_2$	"	38.9	38
$Mo(CO)_5L$	"	26.9	52
$Mo(CO)_5L$	P(t-Bu)Ph_2	57.0	52
trans - $Mo(CO)_4L_2$	PPh_3	50.9	52
$Mo(CO)_5L$	"	37.5	52
trans - $Mo(CO)_4(P^1Bu_3)L$	"	50.9 (P^1)22.0	53
cis - $Mo(CO)_4(P^1Bu_2Ph)L$	"	38.3 (P^1)12.1	53
trans - $Mo(CO)_4(P^1Bu_2Ph)L$	"	51.1 (P^1)27.9	53



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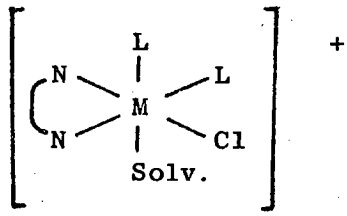

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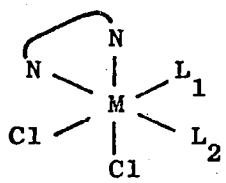

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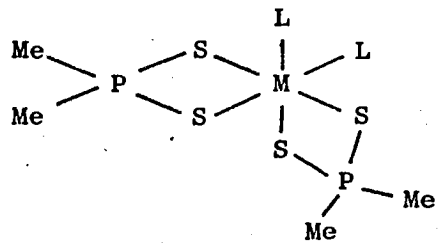

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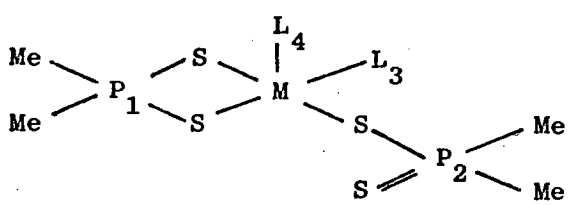

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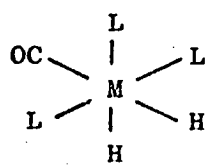
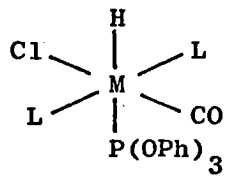


XVII

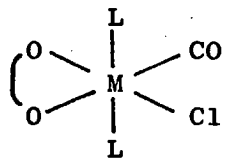
Table 6 ^{31}Chemical Shifts of Monotertiaryphosphine Complexes of RUTHENIUM

Compound	L	S*	δP(ppm)	Ref.
$[RuClBipyL_3]Cl$	PMe_2Ph	XII	6.88(1) 0.33(2)	67
$[RuClBipyL_2]_2Cl_2$	"	XIII	15.1(P_1) 27.2(P_2)	67
$RuCl_2BipyL_2$	"	XIV	29(P_1) 16(P_2)	67
$[RuCl(CH_2Cl_2)phenL_2]Cl$	"	XIII	28(P_1) 16.1(P_2)	67
cis - $Ru(S_2P^1Me_2)_2L_2$	"	XV	21.4 (P^1)88.1	68
$Ru(S_2PMe_2)_2COL_2$	"	XVI	63.5(P_1) 60.7(P_2) 9.5(P_3) -15.8(P_4)	68
$(P^1Ph_3)LClRuCl_3RhClL_2$	PBu_2Ph	-	P^1 40.0 P^1 56.5 (-26.3,-36.0:Rh)	69
RuH_2COL_3	PPh_3	XVIII	44.8(1) 57.2(2)	73
$RuHClL_3$	"	-	94.0(1) 38.4(2)	70
$RuHBrL_3$	"	-	93.8(1) 38.6(2)	
$RuH(CO_2Me)L_3$	"	-	70.8,79.7(1) 43.6,43.5(2)	70,71
$[RuH(MeCN)_2L_3]^+$	PPh_3	-	58.9(1) 46.6(2)	71
$RuCl_2L_3$	"	-	75.7(1) 24.1(2)	70

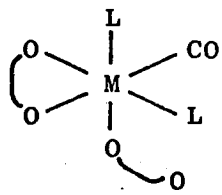
* S - Structure



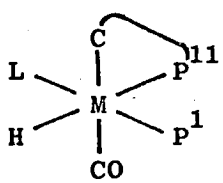
XVIII



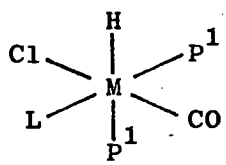
XIX



XX



XXI



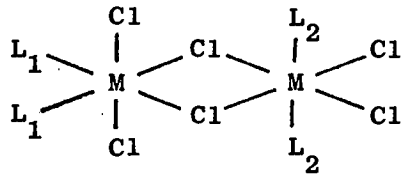
XXII

Table 6 continued

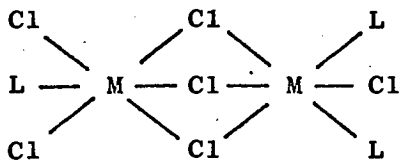
Compound	L	S*	δP(ppm)	Ref.
$RuClBrL_3$	PPh_3	-	79.0(1) 25.9(2)	70
$RuBr_2L_3$	"	-	80.0(1) 27.4(2)	70
$[RuCO(CO_2Me)L_3]^+$	"	-	39.7(1) 29.1(2)	71
$[RuH_2O(MeCN)_2L_3]^+$	"	-	34.9(1) 21.3(2)	71
$RuHClCOP^1(OPh)_3L_2$	"	XVIII	39.5 (P^1)122.1	72
$[RuCl_2L_2]_2$	"	-	58.8 53.0	70
$[RuBr_2L_2]_2$	"	-	61.6 55.0	70
$RuCl(CO_2CF_3)COL_2$	"	XIX	38.55	73
$Ru(CO_2CF_3)_2COL_2$ †	"	XX	42.75	73
trans - $Ru(CO_2CF_3)_2(CO)_2L_2$	"		30.3	73
$RuHCO(P^1(OPh)_3)(P^{11}(OPh)_2(OC_6H_4))L$	PPh_3	XXI	45.1 (P^1)137.5 (P^{11})165.2	72
$RuHClCO(P^1(OPh)_3)_2L$	"	XXII	36.5 (P^1)122.5,129.0	72

*S - Structure

†Spectrum comprises AB pattern at low temperature $^2J_{PP}$= 29.3Hz.



XXIII



XXIV

Table 7 ^{31}P Chemical Shifts of Monotertiaryphosphine Complexes of RHODIUM

Compound	L	δP(ppm)	Ref.
mer - $RhCl_3L_3$	PMe_3	7.6(1) -8.6(2)	74
mer - $RhCl_3L_3$	PEt_3	20.0(1) 4.3(2)	46,74
trans - $RhClCOL_2$	"	23.7,23.6	43,75
mer - $RhCl_3L_3$	PPr_3	14.3,14.9,14.2(1) -0.7,-0.6, 1.1(2)	39,46,74
mer - $RhCl_3L_3$	PBu_3	14.7,15.1,14.7,15.1(1) -0.7,-0.3,-0.7,-0.5(2)	39,46,74,7
mer - $RhBr_3L_3$	"	13.7(1) -7.8(2)	76
$Rh_2Cl_6L_4$	"	37.8	76
$Rh_2Cl_6L_4$ *	"	33.05,36.17(P_1) 2.65, 2.89(P_2)	77
$Rh_2Cl_6L_3$ **	"	53.18(1) 38.24(2)	77
trans - $RhClCOL_2$	"	16.0	43
mer - $RhCl_3(P^1(OMe)_3)L_2$	"	6.5 (P^1)92.9	78
mer - $RhCl_3(P^1(OPh)_3)L_2$	"	6.9 (P^1)78.9	79
trans - $RhClCOL_2$	PMe_2(t-Bu)	17.3	43
trans - $RhClCOL_2$	PEt(t-Bu)	40.7	43
trans - $RhClCOL_2$	PPr_2(t-Bu)	34.6	43

*Structure XXIII: Low frequency value measured in C_6H_6, high frequency in CH_2Cl_2.

**Structure XXIV

Table 7 continued

Compound	L	δP(ppm)	Ref.
trans - $RhClCOL_2$ *	$PMe(\underline{t}\text{-}Bu)_2$	29.0,45.1	51
		ABX pattern A,30.7;B,46.6	
trans - $RhClCOL_2$ *	$PEt(\underline{t}\text{-}Bu)_2$	46.0,51.1	51
		ABX pattern A,47.2;B,58.2	
trans - $RhClCOL_2$ *	$PPr(\underline{t}\text{-}Bu)_2$	43.4,54.7	51
		ABX pattern A,44.5;B,55.9	
trans - $RhClCOL_2$	"	51.6	43
trans - $RhClCOL_2$	$PBu_2(\underline{t}\text{-}Bu)$	35.9	43
mer - $RhCl_3L_3$	PMe_2Ph	4.4,37.7,4.2(1) -5.5,-5.0,-7.0(2)	46,74,80
$[Rh_2Cl_4L_6]^{2+}$	"	-17.7(1) 5.1(2)	80
trans - $RhClCOL_2$	"	-1.1	43
$[RhCl_2(O_2NMe)L_3]^+$	"	-3.8(1) +7.4(2)	80
$[RhCl_2(SFO_3)L_3]^+$	"	-15.3(1) +5.3(2)	80
cis-$Rh(S_2CNMe_2)_2L_2$	"	4.5	81
cis-$Rh(S_2CO)(S_2COEt)L_2$	"	0.46,9.13	81
mer - $RhCl_3L_3$	PEt_2Ph	17.4,17.1,17.5(1) 3.9, 3.9, 3.9(2)	39,46,74
trans - $RhClCOL_2$	"	24.3,24.6	43,75
trans - $RhBrCOL_2$	"	22.9	75
trans - $RhClCO(P^1(OPh)_3)L$	"	26.3 (P^1)119.0	75
trans - $RhClCO(Sb(OCH_2C_6H_4)_3)L$	"	33.3	75

*See pp. 22,23 for discussion.

Table 7 continued

Compound	L	δP(ppm)	Ref.
mer - $RhCl_3L_3$	PPr_2Ph	12.7,12.7(1) -0.4,-0.8(2)	46,74
trans - $RhClCOL_2$	"	16.7	43
mer - $RhCl_3L_3$	PBu_2Ph	12.8,12.7(1) -0.2,-0.7(2)	46,74
trans - $RhClCOL_2$	"	19.6	43
$L_2ClRhCl_3RuClL(P^1Ph_3)$	"	-26.3 }Rh -36.0 (40.0,$P^1$56.5:Ru)	69
trans - $RhClCOL_2$	$P(t\text{-}Bu)_2Ph$	60.0	43
trans - $RhClCOL_2$	$P(t\text{-}Bu)_2$(p-tolyl)	59.0	43
mer - $RhCl_3L_3$	$PMePh_2$	-2.8,-3.4(1) -4.7,-6.8(2)	46,74
trans - $RhClCOL_2$	"	14.3,14.4	43,75
mer - $RhCl_3L_3$	$PEtPh_2$	19.9,20.0(1) 10.1, 9.4(2)	46,74
trans - $RhClCOL_2$	"	2.7,27.1	43,75
trans - $RhBrCOL_2$	"	26.0	75
mer - $RhCl_3L_3$	$PPrPh_2$	16.0(1) 6.8(2)	74
mer - $RhCl_3L_3$	$PBuPh_2$	15.9(1) 7.4(2)	74
$RhClL_3$	PPh_3	48.0,48.9,48.0(1) 31.5,32.2,31.5(2)	76,82,83
$RhBrL_3$	"	46.8(1) 29.8(2)	76
$RhIL_3$	"	43.2(1) 27.1(2)	76
$RhClH_2L_3$	"	20.7(1) 40.3(2)	82
trans - $RhClCOL_2$	"	29.3,29.0,28.9,29.1 29.1,29.1,29.1	39,43,75,76 82,83,84

Table 7 continued

Compound	L	δP(ppm)	Ref.
trans - $RhBrCOL_2$	PPh_3	27.6	75
cis - $RhCl_2(COMe)L_2$	"	29.8	84
trans - $RhCl_2(COMe)L_2$	"	23.6	84
trans - $RhCl_2(CO)MeL_2$	"	18.7	84
$RhCl(C_2H_4)L_2$	"	35.7	82
$RhCl(C_{24}H_{14}O_2)L_2$	"	25.6	85
$RhCl(C_{30}H_{20}O_2)L_2$	"	25.6	85
$RhCl(C_{30}H_{21}O_2N)L_2$	"	26.9	85
$RhCl(C_{22}H_{14}O_2N_2)L_2$	"	25.0	85
$RhCl(C_{26}H_{15}O_2N_3)L_2$	"	26.1	85
$RhCl(C_{24}H_{18}O_2S)L_2$	"	26.3	85
$RhCl(C_{26}H_{14}O_2S)L_2$	"	25.6	85
trans - $RhCl(CO)_2L$	"	24.8	75
trans - $RhClCO(AsPh_3)L$	"	31.45	75
$RhClCODL$	"	30.8	75
$Rh(acac)COL$	"	48.5	75
trans - $RhClCOL_2$	$P(m\text{-tolyl})_3$	29.4	75
$RhClL_3$	$P(p\text{-tolyl})_3$	46.2(1) 30.2(2)	82
$RhClH_2L_3$	"	17.4(1) 37.0(2)	82
$[RhClL_2]_2$	"	49.5	82
trans - $RhClCOL_2$	"	27.3,27.0	82,84
$RhCl(C_2H_2)L_2$	"	33.3	82
$H_2[RhClL_2]_2$	"	51.2(1) 35.2(1)	82
cis - $RhCl_2(COMe)L_2$	"	28.6	84

Table 7 continued

Compound	L	δP(ppm)	Ref.
trans - $RhCl_2(COMe)L_2$	$P(p\text{-tolyl})_3$	22.4	84
trans - $RhCl_2MeCOL_2$	"	17.5	84
cis - $RhCl_2(COMe)L_2$	$P(C_6H_4F)_3$	28.1	84
trans - $RhCl_2(COMe)L_2$	"	21.7	84
trans - $RhCl_2MeCOL_2$	"	16.9	84
trans - $RhClCOL_2$	"	27.0	84

Table 8 ^{31}P Chemical Shifts of Monotertiaryphosphine complexes of PALLADIUM

Compound	L	δP(ppm)	Ref.
PdL_4	PMe_3	-34.8	50
trans - $Pd(P^1(OCH_3)_3)_2L_2$	"	-27.7	32
PdL_4	PEt_3	-1.5	50
$[HPdL_4]^+$	"	3.0(1) 3.0(3)	49
PdL_3	"	9.6	50
$[HPdL_3]^+$	"	A_2B pattern A,20.6;B,10.6	49,59
trans - $PdCl_2L_2$	"	17.8	44
trans - PdI_2L_2	"	8.2	44
trans - $PdCl(P^1F_2O)L_2$	"	25.3 (P^1)63.4	86
trans - $PdCl(P^1FO(OBu))L_2$	"	24.9 (P^1)62.7	86
cis - $[PdCl(P^1F_2O)L]_2$	"	47.7,100.2 (P^1)50.9, 52.3	86
trans - $[PdCl(P^1F_2O)L]_2$	"	46.1,46.8 (P^1)49.5,49.5	86
cis - $PdCl(P^1F_2(OBu))L$	"	47.7 (P^1)not obs.	86
cis - $PdCl_2(P^1F(OBu)_2)L$	"	41.6 (P^1)99.0	86
cis - $PdCl_2(P^1F_2(OPh))L$	"	47.3 (P^1)93.7	86
trans - $PdCl_2L_2$	PPr_3	9.2	44
PdL_3	$P(\underline{iso}\text{-}Pr)_3$	39.0	50
PdL_2	"	49.3	50
PdL_4	PBu_3	-7.9	50
PdL_3	"	-1.4	50

Table 8 continued

Compound	L	δP(ppm)	Ref.
trans - $PdCl_2L_2$	PBu_3	10.0	44
trans - $PdI_2(P^1Me_2Ph)L$	"	-20.6 (P^1) 1.1	87
trans - $PdI_2(P^1(OPh)_3)L$	"	9.8 (P^1)102.8	87
PdL_3	$P(C_6H_{11})_3$	25.9	50
PdL_2	"	38.7	50
PdL_3	$P(C_7H_7)_3$	23	63
trans - $PdCl_2L_2$	PMe_2(t-Bu)	10.7	44
trans - $PdBrL_2$	"	7.8	44
trans - $PdCl_2L_2$	PEt_2(t-Bu)	32.1	44
trans - $PdCl_2L_2$	PPr_2(t-Bu)	26.8	44
trans - $PdBr_2L_2$	"	24.9	44
trans - PdI_2L_2	"	21.1	44
trans - $PdCl_2L_2$	PBu_2(t-Bu)	27.4	44
trans - $PdCl_2L_2$	PPr(t-Bu)$_2$	40.7	44
PdL_4	PMe_2Ph	-20.8	50
trans - $PdCl_2L_2$	"	-5.2	44
cis - $PdCl_2L_2$	"	6.1	44
cis - $PdBr_2L_2$	"	3.9	44
trans - $PdBr_2L_2$	"	-9.5	44
cis - $Pd(N_3)_2L_2$	"	5.2	88,89
trans - $Pd(N_3)_2L_2$	"	-2.0	88,89
$Pd_2Cl_4L_2$	"	15.3	44
trans - $PdI_2(P^1Bu_3)L$	"	1.1 (P^1)-20.6	87
trans - $PdI_2(P^1(OPh)_3)L$	"	-14.7 (P^1) 97.9	87

Table 8 continued

Compound	L	δP(ppm)	Ref.
$PdCl((PhO)_2P^1O)((PhO)_2P^{11}OH)L$	PMe_2Ph	-3.4 (P^1)74.7 (P^{11})95.2	79
cis - $PdCl_2L_2$	PMe_2(p-tolyl)	5.75	89
trans - $PdCl_2L_2$	"	-5.67	89
cis - $Pd(N_3)_2L_2$	"	4.35	89
trans - $Pd(N_3)_2L_2$	"	-3.98	89
cis - $PdCl_2L_2$	$PMe_2(p\text{-}OCH_3C_6H_4)$	5.54	89
trans - $PdCl_2L_2$	"	-6.17	89
cis - $Pd(N_3)_2L_2$	"	4.15	89
trans - $Pd(N_3)_2L_2$	"	-4.50	89
cis - $PdCl_2L_2$	$PMe_2(p\text{-}ClC_6H_4)$	5.72	89
trans - $PdCl_2L_2$	"	-4.86	89
cis - $Pd(N_3)_2L_2$	"	4.57	89
trans - $Pd(N_3)_2L_2$	"	-2.83	89
cis - $PdCl_2L_2$	PEt_2Ph	24.8	44
trans - $PdCl_2L_2$	"	15.7	44
trans - $PdCl(P^1F_2O)L_2$	"	21.6 (P^1)61.8	86
trans - $PdCl(P^1FO(OC_3H_5))L_2$	"	21.6 (P^1)63.6	86
trans - $PdCl(P^1FO(OBu))L_2$	"	21.5 (P^1)62.5	86
cis - $PdCl_2L_2$	PPr_2Ph	19.1	44
trans - $PdCl_2L_2$	"	10.2	44
cis - $PdCl_2L_2$	PBu_2Ph	19.3	44
trans - $PdCl_2L_2$	"	10.8	44
PdL_2	$P(t\text{-}Bu)_2Ph$	67.0	50

Table 8 continued

Compound	L	δP(ppm)	Ref.
trans - $PdCl_2L_2$	$P(t\text{-}Bu)_2Ph$	52.9	44
trans - $PdBr_2L_2$	"	53.4	44
$Pd_2Cl_4L_2$	"	74.5	44
trans - $PdCl_2(py)L$	"	65.0	44
trans - $PdCl_2L_2$	$P(t\text{-}Bu)_2(p\text{-tolyl})$	52.3	44
trans - $PdBr_2L_2$	"	36.6	44
PdL_4	$PMePh_2$	-4.2	50
cis - $PdCl_2L_2$	"	18.9	44
trans - $PdCl_2L_2$	"	7.8	44
trans - PdI_2L_2	"	-5.1	44
cis - $Pd(N_3)_2L_2$	"	17.01	88,89
trans - $Pd(N_3)_2L_2$	"	9.14	88,89
cis - $PdCl_2L_2$	$PMe(p\text{-tolyl})_2$	17.85	89
trans - $PdCl_2L_2$	"	6.25	89
cis - $Pd(N_3)_2L_2$	"	16.19	89
trans - $Pd(N_3)_2L_2$	"	6.82	89
cis - $PdCl_2L_2$	$PMe(p\text{-}ClC_6H_4)_2$	17.78	89
trans - $PdCl_2L_2$	"	7.40	89
cis - $Pd(N_3)_2L_2$	"	16.44	89
trans - $Pd(N_3)_2L_2$	"	7.53	89
cis - $PdCl_2L_2$	$PEtPh_2$	30.0	44
trans - $PdCl_2L_2$	"	19.3	44
trans - $PdCl(P^1F_2O)L_2$	"	24.5 (P^1) 61.2	86
trans - $PdCl(P^1F_2O(OBu))L_2$	"	24.3 (P^1) 63.2	86
cis - $PdCl_2L_2$	$PPrPh_2$	27.4	44
trans - $PdCl_2L_2$	"	16.3	44

Table 8 continued

Compound	L	δP(ppm)	Ref.
cis - $PdCl_2L_2$	$PBuPh_2$	27.1	44
trans - $PdCl_2L_2$	"	16.3	44
trans - $PdCl_2L_2$	$P(t\text{-}Bu)Ph_2$	39.2	44
trans - $PdBr_2L_2$	"	38.0	44
trans - $PdCl_2L_2$	$P(t\text{-}Bu)(p\text{-tolyl})_2$	38.0	44
PdL_4	PPh_3	15.0, 18.4	63,50
PdL_3	"	22.6	50
trans - $PdCl(P^1F_2O)L_2$	"	27.9 (P^1)60.6	86
$PdCl((PhO)_2P^1O)((PhO)_2P^{11}OH)L$	"	23.9 (P^1)73.9 (P^{11})91.5	79
PdL_3	$P(CH_2Ph)_3$	2.7	50

Table 9 ^{31}P Chemical Shifts of Monotertiaryphosphine Complexes of SILVER

Compound	L	δP(ppm)	Ref.
$[AgIL]_4$	PBu_3	-19.0	65
$[AgL_4]^+X$	P(p-tolyl)	5.3 to 4.9	90
AgL_3X	"	10.2	90

$X = PF_6^-$, BF_4^-, ClO_4^-.

Table 10 ^{31}P Chemical Shifts of Monotertiaryphosphine Complexes of CADMIUM

Compound	L	δP(ppm)	Ref.
CdI_2L_2	PEt_3	-10.2	91
CdI_2L_2	PBu_3	-19.7	92
CdI_2L_2	$P(n\text{-}Oct)_3$	-20.0	92
CdI_2L_2	PMe_2Ph	-34.1	91
CdI_2L_2	PEt_2Ph	-11.3	91
CdI_2L_2	$PMePh_2$	-23.9	91
CdI_2L_2	$PEtPh_2$	-10.6	91

Table 11 ^{31}P Chemical Shifts of Monotertiaryphosphine Complexes of TIN

Compound	L	δP(ppm)	Ref.
trans - $SnCl_4L_2$	PEt_3	19.6	93
trans - $SnCl_4L_2$	PBu_3	13.0	92
trans - $SnCl_4L_2$	PEt_2Ph	15.3	93

Table 12 ^{31}P Chemical Shifts of Mono-tertiaryphosphine Complexes of TUNGSTEN

Compound	L	δP(ppm)	Ref.
cis - $W(CO)_2L_4$	PMe_3	37.0(cis-) 34.7(trans-)	31
fac - $W(CO)_3L_3$	"	-37.9	31
mer - $W(CO)_3L_3$	"	-37.5(1) -33.3(2)	31
cis - $W(CO)_4L_2$	"	-37.8,-40.5	31,32
trans - $W(CO)_4L_2$	"	-32.5	31
$W(CO)_5L$	"	-36.3	31
cis - $WCp(CO)_2MeL$	"	-21	94
trans - $WCp(CO)_2MeL$	"	-20	94
trans - $WCp(CO)_2(PbMe_3)L$	"	-16	94
fac - $W(CO)_3L_3$	PBu_3	-14.9	96
cis - $W(CO)_4L_2$	"	-10.0,-10,-9.8	38,95,96
trans - $W(CO)_4L_2$	"	-2.5,-2,-2.6	38,95,96
$W(CO)_5L$	"	-6.4,-6.3	52,96
fac - $W(CO)_3(phen)L$	"	-6.1	96
trans - $W(CO)_4(P^1Ph_3)L$	"	-3.2 (P^1)28.4	53
trans - $W(CO)_4(P^1(OPh)_3)L$	"	-5.3 (P^1)137.0	53
cis - $WCp(CO)_2MeL$	PMe_2Ph	-7	94
trans - $WCp(CO)_2MeL$	"	-5	94
trans - $WCp(CO)_2(PbMe_3)L$	"	-3	94
cis - $W(CO)_4L_2$	PBu_2Ph	-4.0	38
trans - $W(CO)_4L_2$	"	+4.0	38
$W(CO)_5L$	"	-0.8	52
$W(CO)_5L$	$PMePh_2$	-3.8	52

Table 12 continued

Compound	L	δP(ppm)	Ref.
cis - $WCp(CO)_2MeL$	$PMePh_2$	15	94
trans - $WCp(CO)_2MeL$	"	18	94
trans - $WCp(CO)_2(GeMe_3)L$	"	20	94
trans - $WCp(CO)_2(PbMe_3)L$	"	19	94
$W(CO)_5L$	$PEtPh_2$	-12.1	52
$W(CO)_5L$	P(iso-Pr)Ph_2	26.3	52
cis - $W(CO)_4L_2$	$PBuPh_2$	8.2	38
trans - $W(CO)_4L_2$	"	14.4	38
$W(CO)_5L$	"	7.9	52
$W(CO)_5L$	P(t-Bu)Ph_2	41.7	52
$W(CO)_5L$	PPh_3	20.6	52
trans - $W(CO)_4(P^1Bu_3)L$	"	28.4 (P^1)-3.2	53
cis - $WCp(CO)_2MeL$	"	36	94
trans - $WCp(CO)_2MeL$	"	42	94
trans - $WCp(CO)_2(PbMe_3)L$	"	41	94

Table 13 ^{31}P Chemical Shifts of Monotertiaryphosphine Complexes of RHENIUM

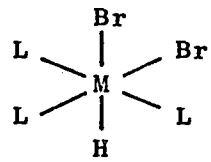
Compound	L	δP(ppm)	Ref.
$Re_2Cl_6L_2$	PBu_3	10	65

Table 14 ^{31}P Chemical Shifts of Monotertiaryphosphine Complexes of OSMIUM

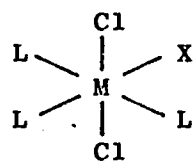
Compound	L	δP(ppm)	Ref.
$OsCl_2COL_3$ *	PMe_2Ph	-46.5(1) -14.5(2)	66
$OsCl_2COL_3$ †	"	-31.9	66
$OsBr_2COL_3$ *	"	-56.3(1) -50.9(2)	66
$OsCl_2(N_2)L_3$ †	"	-36.0	66
$OsCl_2(MeNC)L_3$ *	"	-46.9(1) -41.5(2)	66
$OsCl_2(PhNC)L_3$ *	"	-46.5(1) -40.2(2)	66
$OsCl_2L_3$	PPh_3	-7.2(1) -1.3(2)	70
$OsBr_2L_3$	"	-9.0(1) -0.45(2)	70
mer - $OsHBrCOL_3$	"	-12.3(1) 4.2(2)	70
OsH_2COL_3 (XVII)	"	14.4(1) 18.9(2)	73
mer - $OsH(CO_2C_2F_5)COL_3$	"	0.8(1) 13.9(2)	73
trans - $OsH(CO_2C_2F_5)(CO)_2L_2$	"	12.6	73
$Os(CO_2CF_3)_2COL_2$ (XX)	"	-3.2	73
trans - $Os(CO_2CF_3)_2(CO)_2L_2$	"	8.35	73

* trans - halides

† cis - halides



XXV



XXVI

Table 15 ^{31}P Chemical Shifts of Monotertiaryphosphine Complexes of IRIDIUM

Compound	L	S*	δP(ppm)	Ref.
mer - $IrCl_3L_3$	PMe_3	-	-47.0(1) -42.4(2)	46
IrH_5L	"	-	-51.1	97
mer - IrH_3L_3	PEt_3	-	-8.9(1) -0.1(2)	46,97
mer - $IrHBr_2L_3$	"	XXV	-28.0(1) -46.3(2)	46
mer - $IrCl_3L_3$	"	-	-36.1(1) -33.3(2)	46
mer - $IrCl_2BrL_3$	"	XXVI	-35.2(1) -37.3(2)	46
mer - $IrCl_2IL_3$	"	XXVI	-38.7(1) -43.1(2)	46
mer - $IrBr_3L_3$	"	-	-38.3(1) -42.8(2)	46
mer - IrI_3L_3	"	-	-43.5(1) -56.9(2)	46
IrH_5L	"	-	1.4	97
$H_2L_2IrHClPtClL$	PPr_3	-	-2.2 (-45.0;Pt)	98
mer - $IrCl_3L_3$	PBu_3	-	-40.3(1) -37.7(2)	46
mer - $IrCl_2BrL_3$	"	XXVI	-39.6(1) -43.1(2)	46
mer - $IrCl_2IL_3$	PBu_3	XXVI	-42.5(1) -47.4(2)	46
mer - $IrBr_3L_3$	"	-	-42.6(1) -47.8(2)	46
mer - IrI_3L_3	"	-	-49.1(1) -63.3(2)	46

*S - Structure

Table 15 continued

Compound	L	S**	δP(ppm)	Ref.
trans - $IrClCOL_2$*	$PMe(t\text{-}Bu)_2$	-	22.3 and 36.6	51
			AB pattern(A,22.9;B,39.1)	
trans - $IrClCOL_2$*	$PEt(t\text{-}Bu)_2$	-	38.7,49.0	51
			AB pattern(A,39.1;B,50.9)	
trans - $IrClCOL_2$*	$PPr(t\text{-}Bu)_2$	-	35.9,46.6	51
			AB pattern(A,36.3;B,48.5)	
mer - $IrCl_3L_3$	PMe_2Ph	-	-50.1(1) -40.1(2)	46
mer - $IrCl_2BrL_3$	"	XXVI	-49.6(1) -45.1(2)	46
mer - $IrCl_2IL_3$	"	XXVI	-52.6(1) -51.7(2)	46
mer - $IrCl_2MeL_3$	"	XXVI	-43.8(1) -54.2(2)	46
mer - $IrBr_3L_3$	"	-	-54.6(1) -52.5(2)	46

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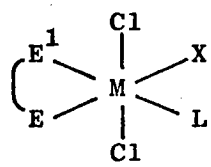
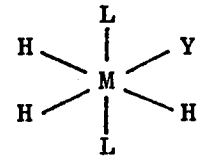
* See pp 22,23 for discussion

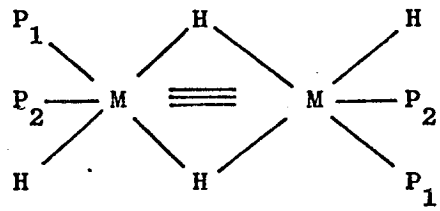
** S - Structure



XXVII



XXVIII



XXIX

Table 15 continued

Compound	L	δP(ppm)	Ref.
mer - IrI_3L_3	PMe_2Ph	-64.7(1) -72.4(2)	46
$IrCl_3(diphos)L^*$	"	-39.6 (P^1) 5.2	99
$IrCl_2Br(diphos)L^*$	"	-43.3 (P^1) 4.4	99
$IrCl_2I(diphos)L^*$	"	-50.0 (P^1) 1.3	99
$IrCl_2N_3(diphos)L^*$	"	-34.5 (P^1) 8.3	99
$IrCl_2NO_3(diphos)L^*$	"	-29.9 (P^1)17.3	99
$IrCl_2NO_2(diphos)L^*$	"	-36.3 (P^1)12.5	99
$IrCl_2NCO(diphos)L^*$	"	-36.5 (P^1)10.9	99
$IrCl_2NCS(diphos)L^*$	"	-42.1 (P^1) 4.2	99
$[IrCl_2py(diphos)L]^{+*}$	"	-34.6 (P^1)10.7	99
$[IrCl_2CO(diphos)L]^{+*}$	"	-41.0 (P^1)19.2	99
$IrCl_3(diars)L^{**}$	"	-39.2	99

* has structure XXVII ; E = P

** has structure XXVII ; E = As

Table 15 continued

Compound	L	S*	δP(ppm)	Ref.
mer - $IrCl_3L_3$	PEt_2Ph	-	-37.5(1) -33.9(2)	46
mer - $IrCl_2BrL_3$	"	XXVI	-37.4(1) -37.4(2)	46
mer - $IrCl_2IL_3$	"	XXVI	-41.2(1) -42.6(2)	46
mer - $IrCl_2NO_3L_3$	"	XXVI	-38.9(1) -23.4(2)	46
mer - $IrBr_3L_3$	"	-	-41.5(1) -44.6(2)	46
mer - IrI_3L_3	"	-	-50.5(1) -60.3(2)	46
$IrH_3(P^1Ph_3)L_2$	"	XXVIII	5.8 (P^1)21.1	97
$IrH_3(AsMe_2Ph)L_2$	"	XXVIII	9.6	97
$IrH_3(SbPh_3)L_2$	"	XXVIII	7.7	97
$IrH_3(P^1(OMe)_3)L_2$	"	XXVIII	6.7 (P^1)129.0	97
$IrH_3(P^1(OMe)_2Ph)L_2$	"	XXVIII	7.0 (P^1)137.7	97
$IrH_3(MeCN)L_2$	"	XXVIII	11.0	97
IrH_5L_2	"	-	1.4	97
trans - $IrClCO(P^1(OPh)_3)L$	"	-	21.4 (P^1)110.5	75
mer - $IrCl_3L_3$	PPr_2Ph	-	-41.6(1) -38.3(2)	46

* S - Structure

Table 15 continued

Compound	L	S*	δP(ppm)	Ref.
mer - $IrCl_3L_3$	$PMePh_2$	-	-55.2(1) -47.1(2)	46
mer - $IrCl_2BrL_3$	"	XXVI	-56.9(1) -47.3(2)	46
mer - $IrCl_2IL_3$	"	XXVI	-63.6(1) -56.1(2)	46
trans - $IrClCOL_2$	$PEtPh_2$	-	21.9	75
$[IrH_2L_2]_2$	PPh_3	XXIX	15.3(P_1) 18.5(P_2^1)	100
trans - $IrClCOL_2$	"	-	23.9	75
trans - $IrBrCOL_2$	"	-	22.4	75
trans - $Ir(C_6H_5)COL_2$	"	-	24.22	101
trans - $Ir(2\text{-}C_6H_4CH_3)COL_2$	"	-	24.32	101
trans - $Ir(3\text{-}C_6H_4CH_3)COL_2$	"	-	24.93	101
trans - $Ir(4\text{-}C_6H_4CH_3)COL_2$	"	-	23.52	101
trans - $Ir(2\text{-}C_6H_4OCH_3)COL_2$	"	-	24.73	101
trans - $Ir(4\text{-}C_6H_4N(CH_3)_2)COL_2$	"	-	28.82	101
trans - $Ir(3\text{-}C_6H_4Cl)COL_2$	"	-	24.63	101
trans - $Ir(4\text{-}C_6H_4Cl)COL_2$	"	-	24.53	101
trans - $Ir(3\text{-}C_6H_4CF_3)COL_2$	"	-	24.42	101
trans - $Ir(4\text{-}C_6H_4CF_3)COL_2$	"	-	24.93	101
trans - $Ir(2,6\text{-}C_6H_4(OCH_3)_2)COL_2$	"	-	23.72	101
trans - $Ir(C_6F_5)COL_2$	"	-	23.62	101
$IrH_3(P^1Et_2Ph)_2L$**	"		21.2 (P^1) 5.8	97

*S - Structure

** has structure XXVIII, Y = PPh_3, L = P^1Et_2Ph.

Table 16 ^{31}P Chemical Shifts of Monotertiaryphosphine Complexes of PLATINUM

Compound	L	δP(ppm)	Ref.
fac - $PtMe_3IL_2$	PMe_3	-54.4	102
$[PtHL_4]^+$	PEt_3	-20.8(1) -17.4(3)	49
$[PtHL_3]^+$	"	16.3,16.6,17.0(1) 13.4,13.4,13.7(2)	49,59,103
trans - $PtHClL_2$	"	23.3,23.2	14,104
trans - $PtHBrL_2$	"	20.8,21.8	14,104
trans - $PtHIL_2$	"	19.7,19.8	14,104
trans - $PtHCNL_2$	"	19.9,20.3	14,104
trans - $PtHN_3L_2$	"	23.2	104
trans - $PtHNO_2L_2$	"	21.8,22.0	14,104
trans - $PtHNO_3L_2$	"	26.5,26.5	14,104
trans - $PtHNCOL_2$	"	22.5	104
trans - $PtHNCSL_2$	"	22.5,23.1	14,104
trans - $PtHSCNL_2$	"	20.2,20.8	14,104
trans - $[PtH(P^1Ph_3)L_2]^+$	"	A_2B pattern(A,16.0;B,20.1)	103
cis - $PtCl_2L_2$	"	9.6	40
trans - $PtCl_2L_2$	"	12.3	40
cis - $PtClMeL_2$	"	14.6(A) 8.7(B)	105
trans - $PtClMeL_2$	"	14.5,16.2	102,105
cis - $PtClPhL_2$	"	9.2(A) 3.1(B)	105
trans - $PtClPhL_2$	"	13.6	105
cis - $PtBrMeL_2$	"	12.9(A) 10.9(B)	105

(A) - trans- to Me

(B) - trans- to Cl

Table 16 continued

Compound	L	δP(ppm)	Ref.
trans - $PtBrMeL_2$	PEt_3	13.9	105
trans - $PtIMeL_2$	"	9.4,10.8	102,105
cis - $PtMe_2L_2$	"	9.7	105
cis - $PtMeN_3L_2$	"	16.8(A) 6.7(B)	105
trans - $PtMeN_3L_2$	"	17.9	105
trans - $PtMeCNL_2$	"	13.9	105
trans - $PtMeNO_2L_2$	"	14.7	105
trans - $PtMeNO_3L_2$	"	21.0	105
trans - $PtMeNCOL_2$	"	15.9	105
cis - $PtMeNCSL_2$	"	15.5(A) 4.3(B)	105
trans - $PtMeNCSL_2$	"	16.9	105
cis - $PtPh_2L_2$	"	3.5	105
trans - $PtPh_2L_2$	"	8.0	105
cis - $P(Mes)BrL_2$	"	8.3(A) 0.8(B)	105
trans - $PtCl_2Me_2L_2$	"	-7.7	105
trans - $PtI_2Me_2L_2$	"	-23.4,-22.8	102,105
trans - $Pt((EtO)_2P^1O)_2L_2$	"	17.0 (P^1)73.9	79
trans - $Pt((PhO)_2P^1O)_2L_2$		15.6 (P^1)69.5	79
trans - $PtCl((PhO)_2P^1O)L_2$	"	21.1 (P^1)30.1	79
cis - $PtCl_2(P^1Bu_3)L$	"	9.5 (P^1) 1.2	106

(A) - trans- to Me

(B) - trans- to Cl

Table 16 continued

Compound	L	δP(ppm)	Ref.
trans - $PtCl_2(P^1Bu_3)L$	PEt_3	$^{12.7}_{(P^1)4.9}$	106
cis - $PtCl_2(P^1(OPh)_3)L$	"	$^{16.5}_{(P^1)62.7}$	106
$PtCl((MeO)_2P^1O)((MeO)_2P^{11}OH)L$	"	$^{18.3}_{(P^1)55.1}$ $(P^{11})92.7$	79
$PtCl((PhO)_2P^1O)((PhO)_2P^{11}OH)L$	"	$^{17.1}_{(P^1)48.2}$ $(P^{11})87.2$	79
cis - $[PtCl(P^1F_2O)L]_2$	"	$^{23.0,22.9}_{(P^1)93.6,\ 1.1}$	86
cis - $PtCl_2(P^1F_2(OBu))L$	"	$^{19.8}_{(P^1)72.3}$	86
cis - $PtCl_2(P^1F_2(OPh))L$	"	$^{20.8}_{(P^1)69.9}$	86
cis - $PtCl_2L$	PPr_3	-0.2	40
trans - $PtCl_2L_2$	"	3.8	40
$[PtClL_3]^+$	PBu_3	12.8,1.1(1) 15.7,10.9(2)	105,106
cis - $PtCl_2L$	"	1.2,1.4,1.4,0.9	40,41,95,105
trans - $PtCl_2L_2$	"	5.1,4.9,4.9,4.3	40,41,95,105
cis - $PtBr_2L_2$	"	0.8	41
trans - $PtBr_2L_2$	"	0	41
cis - PtI_2L_2	"	-1.1	41
trans - PtI_2L_2	"	-7.9	41
trans - $Pt(CN)_2L_2$	"	5.9	41
$[PtCl(P^1Me_2Ph)L_2]Cl$	"	$^{8.5}_{(P^1)-14.3}$	106
$Pt((EtO)_2P^1O)_2L_2$	"	$^{9.7}_{(P^1)72.7}$	79
$Pt((BuO)_2P^1O)_2L_2$	"	$^{11.0}_{(P^1)71.8}$	79

Table 16 continued

Compound	L	δP(ppm)	Ref.
trans - $PtCl((MeO)_2P^1O)L_2$	PBu_3	13.8 (P^1)35.2	79
trans - $PtCl((PhO)_2P^1O)L_2$	"	12.8 (P^1)30.2	79
trans - $PtBr((PhO)_2P^1O)L_2$	"	9.7 (P^1)29.8	79
trans - $PtI((PhO)_2P^1O)L_2$	"	6.2 (P^1)28.4	79
trans - $PtN_3((PhO)_2P^1O)L_2$	"	16.3 (P^1)30.5	79
trans - $PtCN((PhO)_2P^1O)L_2$	"	8.4 (P^1)65.7	79
trans - $PtNO_2((PhO)_2P^1O)L_2$	"	11.6 (P^1)21.9	79
trans - $PtNO_3((PhO)_2P^1O)L_2$	"	18.9 (P^1) 8.2	79
trans - $PtNCO((PhO)_2P^1O)L_2$	"	13.6 (P^1)29.0	79
trans - $PtNCS((PhO)_2P^1O)L_2$	"	14.6 (P^1)25.7	79
trans - $PtOCOMe((PhO)_2P^1O)L_2$	"	16.3 (P^1)22.2	79
trans - $Pt_2Cl_4L_2$	"	2.3	41
cis - $PtCl_4L_2$	"	12.5	41
trans - $PtCl_4L_2$	"	0	41
cis - $PtCl_2(P^1Et_3)L$	"	1.2 (P^1) 9.5	106
trans - $PtCl_2(P^1Et_3)L$	"	4.9 (P^1)12.7	106
cis - $PtCl_2(P^1Me_2Ph)L$	"	1.0 (P^1)-14.8	106
trans - $PtCl_2(P^1Me_2Ph)L$	"	5.2 (P^1)-8.0	106

Table 16 continued

Compound	L	δP(ppm)	Ref.
cis - $PtCl_2(P^1Ph_3)L$	PBu_3	-2.5 (P^1)11.9	106
trans - $PtCl_2(P^1Ph_3)L$	"	6.3 (P^1)20.8	106
cis - $PtCl_2(P^1(OMe)_3)L$	"	8.5 (P^1)70.8	106
$[PtCl(P^1(OPh)_3)L_2]^+$	"	15.7,26.9 (P^1)65.3,67.3	79,106
cis - $PtCl_2(P^1(OPh)_3)L$	"	7.8,7.8 (P^1)59.8,62.8	79,106
trans - $PtCl_2(P^1(OPh)_3)L$	"	4.6,4.6 (P^1)88.3,88.9	79,106
trans - $PtCl_2(P^1Ph_2H)L$	"	3.5 (P^1)-10.7	106
cis - $PtCl_4(P^1(OPh)_3)L$	"	25.4 (P^1)10.9	106
cis - $PtClMe(P^1(OPh)_3)L$	"	12.0 (P^1)77.6	79
cis - $PtMe_2(P^1(OPh_3)L$	"	3.6 (P^1)104.7	79
$PtCl((PhO)_2P^1O)((PhO)_2P^{11}OH)L$	"	11.6 (P^1)48.3 (P^{11})88.0	79
trans - $PtBr_2(EtNH_2)L$	"	-9.5	41
trans - $PtI_2(EtNH_2)L$	"	-10.5	41
trans - $PtCl_2(Et_2NH)L$	"	-6.5	41
trans - $PtBr_2(Et_2NH)L$	"	-8.7	41
trans - $PtI_2(Et_2NH)L$	"	-11.6	41
trans - $PtCl_2pyL$	"	-8.0	41
trans - $PtBr_2pyL$	"	-11.7	41
trans - PtI_2pyL	"	-14.7	41
cis - $PtCl_2(Me_2S)L$	"	2.2	41

Table 16 continued

Compound	L	δP(ppm)	Ref.
PtL_4	$P(C_7H_7)_3$	11	63
PtL_3	"	51	63
cis - $PtCl_2L_2$	PMe_2Ph	-15.2,-16.2	40,102
cis - $PtBr_2L_2$	"	-16.1	102
cis - PtI_2L_2	"	-18.2	102
trans - PtI_2L_2	"	-24.0	102
cis - $PtMeClL_2$	"	-6.3(A) -15.0(B)	102
trans - $PtMeClL_2$	"	-2.95	102
trans - $PtMeBrL_2$	"	-5.5	102
trans - $PtMeIL_2$	"	-9.7	102
cis - $PtMe_2L_2$	"	-12.5	102
trans - $PtCF_3IL_2$	"	-10.2	102
trans - $PtMe(SePh)L_2$	"	-2.9	102
trans - $Pt(SPh)_2L_2$	"	-7.5	102
trans - $Pt(SePh)_2L_2$	"	-12.5	102
trans - $Pt(CH=CHPh)_2L_2$*	"	-10.60,-11.80	107
trans - $Pt(CH=CHCH_2OMe)_2L_2$	"	-10.20	107
trans - $Pt(CH=CHCMe_2OH)_2L_2$*	"	-9.80,-9.93	107
trans - $Pt(CH=CHC_6H_{10}OH)_2L_2$*	"	-10.65,-11.80	107
cis - $Pt(CH_2)_4L_2$	"	-11.6	102

A - trans- to Me

B - trans- to Cl

* - mixture of rotational isomers

Table 16 continued

Compound	L	δP(ppm)	Ref.
$PtMe_2Cl_2L_2$ **	PMe_2Ph	-13.8,-39.5	102
fac-$PtMe_3ClL_2$	"	-37.2	102
$PtMe_2PrClL_2$ **	"	-38.2,-34.9	102
$PtBr_3MeL_2$	"	-23.8	102
$PtMe_2Br_2L_2$	"	-20.0	102
fac-$PtMe_3BrL_2$	"	-40.5	102
$PtMe_2PrBrL_2$ *	"	-40.3, 36.8	102
$PtMe_2(PhCH_2)BrL_2$	"	-37.2	102
$PtMe_2I_2L_2$	"	-30.5	102
fac-$PtMe_3IL_2$	"	-46.1	102
$PtMe_2(CF_3)IL_2$ *	"	-45.9,-44.6	102
cis-$PtCl_2(P^1Bu_3)L$	"	$^{-14.8}_{(P^1)\ 1.0}$	106
trans-$PtCl_2(P^1Bu_3)L$	"	$^{-8.0}_{(P^1)\ 5.2}$	106
$[PtCl(P^1Bu_3)_2L]^+$	"	$^{-14.5}_{(P^1)\ 8.5}$	106
$LClPtCl_2PtClL$	"	-19.6	102
$LClPt(SMe)_2PtClL$	"	-14.8	102
$LClPt(SPh)_2PtClL$	"	-12.6	102
$LMePt(SMe)_2PtMeL$	"	-13.2	102
cis-$PtCl_2L_2$	PEt_2Ph	3.3	40
trans-$PtCl_2L_2$	"	11.3	40
trans-$PtCl(P^1F_2O)L_2$	"	$^{20.5}_{(P^1)34.5}$	86

* - mixture of rotational isomers

** - isomeric mixture

Table 16 continued

Compound	L	δP(ppm)	Ref
cis-$PtCl_2L_2$	PPr_2Ph	-2.7	40
trans-$PtCl_2L_2$	"	6.3	40
cis-$PtCl_2L_2$	PBu_2Ph	-2.3	40
trans-$PtCl_2L_2$	"	6.5	40
cis-$PtCl_2L_2$	$PMePh_2$	-1.2,-2.2,-1.2	40,102,108
trans-$PtClMeL_2$	"	13.2	108
cis-PtI_2L_2	"	-5.1	102
trans-PtI_2L_2	"	-8.0	102
trans-$PtIMeL_2$	"	7.9	102
cis-$PtMe_2L_2$	"	5.3,6.4	102,108
fac-$PtMe_3IL_2$	"	-36.3	102
cis-$PtCl_2L_2$	$PEtPh_2$	9.8	40
trans-$PtCl(P^1F_2O)L_2$	"	20.5 (P^1)34.5	86
cis-$PtCl_2L_2$	$PPrPh_2$	6.9	40
cis-$PtCl_2L_2$	$PBuPh_2$	7.0	40
trans-$PtCl_2L_2$	"	12.0	33
PtL_3	PPh_3	55	63
$[PtHL_3]^+$	"	A_2B pattern(A,-3;B-2.4)	103
$PtC_2H_4L_3$	"	11.4	109
$[Pt(CH_2\text{-}C_6H_4\text{-}CN)L_3]^+$	"	18.3(1) 21.9(2)	111
$Pt(HC{\equiv}CCHMeOH)L_2$	"	28.1,26.7	10
$Pt(HC{\equiv}CCHPhOH)L_2$	"	26.8,25.4	110
$Pt(PhC{\equiv}CCMeMeOH)L_2$	"	26.6,23.6	110
$Pt(HOCH_2C{\equiv}CCH_2OH)L_2$	"	26.4	110

Table 16 continued

Compound	L	δP(ppm)	Ref.
$Pt(HOCMe_2C{\equiv}CCMe_2OH)L_2$	PPh_3	23.8	110
$Pt(CO.O.CH_2C^1{=}CH(CH_2OH))L_2$	"	26.0,26.2	110
$Pt(CO.O.CHMeC{=}CH_2)L_2$	"	25.4,26.2	110
$Pt(CO.O.CMe_2C{=}CH_2)L_2$	"	26.0,26.1	110
$Pt(CO.O.CMeEtC{=}CH_2)L_2$	"	26.2,26.4	110
Pt(CYCLOHEXYLIDENE)L_2	"	26.0,26.4	110
$Pt(CF_2{=}CF_2)L_2$	"	25.7	102
$Pt(CF_3C{\equiv}CCF_3)L_2$	"	19.7	102
trans-$PtCl(P^1F_2O)L_2$	"	23.8 (P^1)not.obs.	86
cis-$PtCl(CH_2C_6H_4CN)L_2$	"	22.0(A) 21.2(B)	(111)
trans-$PtCl(CH_2C_6H_4CN)L_2$	"	25.8	(111)
cis-$PtBr(CH_2C_6H_4CN)L_2$	"	19.5(A) 20.4(B)	(111)
trans-$PtBr(CH_2C_6H_4CN)L_2$	"	25.8	(111)
trans-$PtN_3(CH_2C_6H_4CN)L_2$	"	25.7	111
$[Pt(CH_2C_6H_4CN)L_2]^+$	"	19.1(A) 12.9	111
trans-$PtCl(COCH_2C_6H_4CN)L_2$	"	19.7	111
trans-$PtBr(COCH_2C_6H_4CN)L_2$	"	18.7	111
cis-$Pt(CH_2C_6H_4C(OCH_3)NH)L_2$	"	27.3(A) 16.0	111
cis-$PtMe(SnMe_2Cl)L_2$	"	32.1(A) 21.6	112
cis-$PtPh(SnMe_2Cl)L_2$	"	26.2(A) 21.8	112
cis-$PtPh(SnMePhCl)L_2$	"	26.7(A) 22.7	112
cis-$PtPh(SnPh_3)L_2$	"	25.8(A) 20.7	112

A - trans-to R

B - trans-to halide

Table 16 continued

Compound	L	δP(ppm)	Ref.
cis-$PtPh(SnPh_2Cl)L_2$	PPh_3	26.2(A) 22.5	112
cis-$PtPh(SnPh_2Br)L_2$	"	25.9(A) 23.9	112
cis-$PtPh(SnPh_2I)L_2$	"	24.1(A) 24.8	112
cis-$PtPh(SnPh_2OH)L_2$	"	27.1(A) 21.3	112
cis-$PtPh(SnPh_2ONO_2)L_2$	"	26.1(A) 15.7	112
cis-$Pt(m\text{-}CH_3C_6H_4)(Sn(m\text{-}CH_3C_6H_4)_2Cl)L_2$	"	28.1(A) 23.6	112
$[PtH(P^1Et_3)_2L]^+$	"	A_2B pattern(A,16.5;B,20.1)	103
cis-$PtCl_2(P^1Bu_3)L$	"	11.9 (P^1)-2.5	106
trans-$PtCl_2(P^1Bu_3)L$	"	20.8 (P^1) 6.3	106
cis-$PtCl_2(P^1(OPh)_3)L$	"	17.3 (P^1)54.6	106

A - trans- to R

Table 17 ^{31}P Chemical Shifts of Monotertiaryphosphine Complexes of MERCURY

Compound	L	δP(ppm)	Ref.
$HgCl_2L_2$	PBu_3	29.0,31.0	113,92
$HgBr_2L_2$	"	56.9,22.6,23.0	20,113,92
HgI_2L_2	"	10.4,10.5	113,92
$Hg(SCN)_2L_2$	"	33.5	92
$Hg(CN)_2L_2$	"	27.0	92
$Hg_2Cl_4L_2$	"	34.4,34.5	113,92
$Hg_2Br_4L_2$	"	27.6,28.5	113,92
HgI_4L_2	"	7.3 and 19.4,† 16.5	113,92
$HgCl_2L_2$	$P(n\text{-Oct})_3$	29.0	92
$HgBr_2L_2$	"	22.5	92
HgI_2L_2	"	10.0	92
$Hg_2Cl_4L_2$	"	33.0	92
$Hg_2Br_4L_2$	"	30.5	92
$Hg_2I_4L_2$	"	16.5	92
$Hg_2Cl_4L_2$	PEt_2Ph	43.2	113
$Hg_2Br_4L_2$	"	35.6	113
$Hg_2I_4L_2$	"	12.2,21.5†	113
$HgCl_2L_2$	PBu_2Ph	28.6	113
$HgBr_2L_2$	"	48.3,22.1	20,113
HgI_2L_2	"	6.1	113
$Hg_2Cl_4L_2$	"	36.5	113
$Hg_2Br_4L_2$	"	29.0	113
$Hg_2I_4L_2$	"	6.4 and 16.4†	113

† Two isomers in equilibrium in solution.

Table 17 continued

Compound	L	δP(ppm)	Ref.
$HgCl_2L_2$	$PBuPh_2$	26.4	113
$HgBr_2L_2$	"	19.3	113
HgI_2L_2	"	4.0	113
$Hg_2Br_4L_2$	"	36.4,27.0	20,113

CHAPTER TWO

SYNTHESES AND REARRANGEMENT REACTIONS OF SOME MONOTERTIARYPHOSPHINE COMPLEXES OF RUTHENIUM

2.1 Introduction

In the last fifteen years a substantial amount of work has been published on the syntheses and reactions of tertiary phosphine complexes of ruthenium. In particular the reactions of tertiary phosphines with hydrated ruthenium trichloride have received considerable attention. These studies clearly indicate that the reaction products are very dependent upon such variables as the nature and amount of phosphine employed, the time of reaction, the temperature and the solvent media.

Thus when commercial hydrated ruthenium trichloride "$RuCl_3.3H_2O$" is refluxed under nitrogen with a sixfold excess of triphenylphosphine in either methanol,[114,115] ethanol[115] or isopropanol[115] for several hours, then red-brown crystals of the monomeric complex $RuCl_2(PPh_3)_3$ are produced. In contrast, shaking the two reactants (in the same molar ratios) in methanol produces the brown tetrakis phosphine complex.[114]

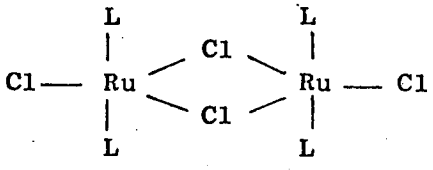
Rather surprisingly, refluxing a mixture of "$RuCl_3.3H_2O$" and tri-p-tolylphosphine in methanol gives the tetrakis complex. This may be converted to the tris complex only by prolonged treatment with hydrogen chloride gas.[116]

However, when a 1:2 molar ratio of "$RuCl_3.3H_2O$" and triphenylphosphine is shaken in methanol for several days, green crystals of the ruthenium(III) complex $RuCl_3(PPh_3)_2MeOH$[114,117] are deposited. As stated above, these reactions are sensitive both to the amount of phosphine and the volume of solvent used; thus reactions involving shaking "$RuCl_3.3H_2O$" with intermediate molar ratios of triphenylphosphine or reactions in which large volumes of solvent are used, produce mixtures of the ruthenium(III) and ruthenium(II) species.

"$RuBr_3$" (produced by shaking "$RuCl_3.3H_2O$" with LiBr in a 1:6

ratio) can be used to synthesise the corresponding bromo- compounds.[114]†

When commercial ruthenium trichloride is refluxed in either isobutanol or cychlohexanol with triphenylphosphine, the only product obtained is the black, insoluble $[RuCl_2(PPh_3)_2]_n$.[115] This product is also obtained from refluxing $RuCl_2(PPh_3)_3$ in methylethylketone.[118] When $RuCl_2(PPh_3)_3$ is refluxed in acetone under nitrogen, a red crystalline solid analysing for $RuCl_2(PPh_3)_2$.acetone is precipitated,[118] whose far infra-red spectrum is virtually identical to $[RuCl_2(PPh_3)_2]_n$ and shows the presence of both terminal (ν_{Ru-Cl} 323 cm^{-1}) and bridging (ν_{Ru-Cl} 250 cm^{-1}) chloro groups supporting the original formulation as (XXX):



(XXX)

However, if the reaction between "$RuCl_3.3H_2O$" and excess (6 to 12 fold) triphenylphosphine is carried out under reflux in 2-methoxyethanol, reductive decarbonylation of the solvent occurs with precipitation of the complex $RuHClCO(PPh_3)_3$[115,119] (ν_{Ru-H} 2020 cm^{-1}; ν_{CO} 1916, 1900 cm^{-1}), whereas when 2-ethoxyethanol, iso-amylalcohol or n-butanol are used as solvents, $RuCl_2CO(PPh_3)_2$[115] (ν_{CO} 1978, 1960 sh. cm^{-1}) is the reported product. (These latter reactions will be discussed further in Chapter 4).

Reductive decarbonylation also occurs in the reaction of excess tricyclohexylphosphine with hydrated ruthenium trichloride in 2-methoxyethanol. In this case the five coordinate complexes $RuHClCO(PCy_3)_2$[120,121] (ν_{Ru-H} 2030 w. cm^{-1}; ν_{CO} 1905 cm^{-1}; ν_{Ru-Cl} 337 cm^{-1})

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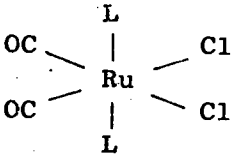
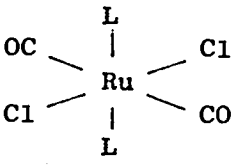
† see page 184

and $RuCl_2CO(PCy_3)_2$ [122] (ν_{CO} 1930 cm^{-1}; ν_{Ru-Cl} 335 cm^{-1}) are obtained. These complexes react readily with pyridine and carbon monoxide respectively to produce $RuHClCO(PCy_3)_2py$ (ν_{Ru-H} 2038 w. cm^{-1}; ν_{CO} 1881 cm^{-1}) and $RuCl_2(CO)_2(PCy_3)_2$ (the cis - complex XXXI (ν_{CO} 2035 cm^{-1}, 1965 cm^{-1}; ν_{Ru-Cl} 305 cm^{-1}, 227 cm^{-1}) is formed when the reaction is performed in benzene solution and the trans - isomer XXXII (ν_{CO} 1984 cm^{-1}; ν_{Ru-Cl} 345 cm^{-1}, 334 cm^{-1}) when CO is reacted with solid $RuCl_2CO(PCy_3)_2$.). Neither of the five coordinate complexes



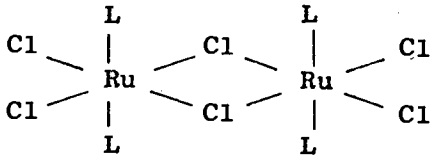
XXXI



XXXII

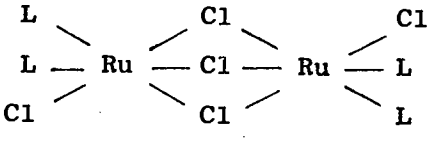
however will react with excess PCy_3 to give the corresponding six coordinate complexes observed as the sole products in the case of triphenylphosphine. This difference in behaviour between triphenylphosphine and tricyclohexylphosphine is probably due to the larger Tolman cone angle of PCy_3(179°) compared to PPh_3(145°).[58]

In contrast when "$RuCl_3.3H_2O$" is shaken in ethanol with PBu^n_3 or PPr^n_3 (in a 1:2.2 molar ratio) for 72 hours, the ruthenium(III) dimeric compound $[RuCl_3L_2]_2$ (XXXIII), and a mixed ruthenium(II)/



XXXIII

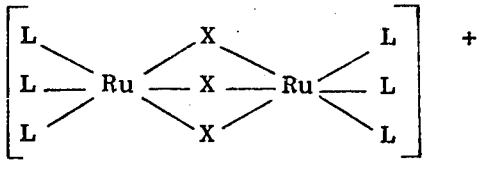
ruthenium(III) species $Ru_2Cl_5L_4$ (XXXIV) are isolated.[123,124,125]



XXXIV

Monomeric ruthenium(III) compounds of the type $RuCl_3L_3$ ($L = PR_2Ph$; R = Me, Et, n-Bu, Ph)[126,127] may be prepared by refluxing hydrated ruthenium trichloride and the tertiaryphosphine (1:4 molar ratio) in an ethanol/HCl mixture for five minutes. These complexes have been shown to have the meridional configuration.

However, in contrast to these reactions, refluxing a range of alkyldiaryl, dialkylaryl or trialkyl phosphines with "$RuX_3.3H_2O$" (X = Cl,Br,I) in aqueous ethanol[128] (in the absence of acid) or in 2-methoxyethanol,[129] gives the lemon-yellow, ionic compounds $[Ru_2X_3L_6]X$ ($L = PMe_2Ph, PEt_2Ph, PPr_2Ph, PBu_2Ph, PEt_3, PMePh_2, PEtPh_2$) (XXXV) which contain a triple halide bridge.



XXXV

These dimers do not react with excess of tertiary phosphine to produce the corresponding monomeric complexes RuX_2L_4[126]. The halide bridges can however be cleaved by prolonged shaking with carbon monoxide in ethanol at 20°C to give the corresponding monocarbonyl species, RuX_2COL_3 (ν_{CO} 1942 cm^{-1}, X = Cl: ν_{CO} 1948 cm^{-1}, 1916 cm^{-1}, X = Br: ν_{CO} 1943 cm^{-1}, X = I), (L = PEt_2Ph,) and with ethanolic KOH to give the hydrido-carbonyl complex $RuHXCOL_3$ (ν_{CO} 1910 cm^{-1} X = Cl: ν_{CO} 1915 cm^{-1}, X = Br: ν_{CO} 1929 cm^{-1}, X = I) L = PEt_2Ph.[126]

Bridge cleavage can also occur by reaction with ditertiary-phosphines, 2,2'-bipyridyl(bipy) and 1,10-phenanthroline(phen), slowly in ethanolic solution or more rapidly in a melt to give the corresponding RuX_2(ditertiaryphosphine)$_2$, RuX_2L_2(bipy) and RuX_2L_2(Phen)[L = PEt_2Ph] respectively.[128]

Although a general preparative method for monomeric mono-tertiary phosphine halide complexes of ruthenium(II) of type RuX_2L_{3or4} has proved elusive, the corresponding hydrido species RuH_2L_4 have been prepared by reaction of the ionic dimer with mixtures of hydrogen gas and hydrazine (L = $PMePh_2$)[130] or with $NaBH_4$ or $LiAlH_4$ (L = PMe_2Ph).[131]

Attempts have been made to prepare the monomeric tertiary phosphine halide complexes by reaction of the hydrido complexes with CCl_4, which had been shown to convert the analogous tertiary phosphite complex $RuH_2(P(OEt)_3)_4$ to the corresponding $RuCl_2(P(OEt)_3)_4$. However in the phosphine case, only the hydrido chloro complex $RuHCl(PMe_2Ph)_4$[131] was produced. Similarly, treatment of $RuH_2(PMe_2PH)_4$ with HCl[130] produced the ionic dimer $[Ru_2Cl_3L_6]Cl$ and not the desired monomer

It is also interesting to note that although analogous triple halide bridged dimeric cations can be prepared for phosphinites ($P(OR)Ph_2$), phosphonites ($P(OR)_2Ph$)[132] and phosphites $P(OR)_3$[133] (R = Me,Et) by reaction of $[RuX_2C_7H_8]_n$ with an excess of ligand and $NaBPh_4$ in methanol, there was until very recently[134] no evidence for the formation of these compounds with such ligands as secondary phosphines, ditertiaryphosphines, mono and ditertiaryarsines and triphenylstibine. Reactions of "$RuX_3.3H_2O$" with these ligands produce the monomeric complexes of the type found with triphenylphosphine:
RuX_2L_3 when X = Cl; L = $SbPh_3$;[114] X = Cl,Br; L = $AsPh_3$.[135]
RuX_2L_4 when X = Cl,Br; L = $AsMe_2Ph$,[126] $AsMePh_2$, $AsMe_2Bz$,[136] $PHPh_2$,[137] L_2 = ditertiaryphosphine[128,138,139,140] or arsine;[141,142] X = Br; L = $SbPh_3$.[143]

Recently however Leelamani and Reddy[134] have obtained the yellow $[Ru_2Cl_3(AsEtPh_2)_6]Y$ (Y = Cl,ClO_4^-, BF_4^-, BPh_4^-) from the reaction of ruthenium trichloride with a sixfold excess of ligand in

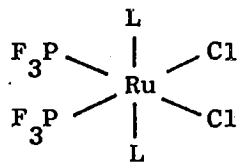
ethanol. The complexes $RuCl_2(AsEtPh_2)_{3or4}$ could not be isolated. The same reaction with $AsMePh_2$ however produces only $RuCl_2(AsMePh_2)_4$.

It therefore seems somewhat surprising that little conclusive evidence for the formation of monomeric halide complexes of mono-tertiary-phosphines with ruthenium has been found. It had been noted previously[144] that the reaction between $RuCl_2(PPh_3)_3$ and neat PEt_3 gave a green oil. It was suggested that this might contain $RuCl_2(PEt_3)_3$. However, attempts to isolate this product by treatment of the oil with dichloromethane gave only the yellow dimer $[Ru_2Cl_3(PEt_3)_6]Cl$.

Chatt et al[145] also investigated the reaction of mer - $RuX_3(PMe_2Ph)_3$ with secondary and tertiary amines in dry ethanolic solution, in the absence of air. This reaction yielded the yellow ethanolates $RuX_2(PMe_2Ph)_3EtOH$ (ν_{OH}EtOH ca 3,500 cm^{-1} sharp), which are unstable in the solid state and in solution, forming a green product which is said to be $RuX_2(PMe_2Ph)_3$, although no spectroscopic or analytical information is given for the latter complex.

When "$RuCl_3.3H_2O$" is treated with $PBzMe_2$ the red monomeric complex $RuCl_2L_4$[136] is formed, which slowly turns green over a period of months. Apart from the proton nmr spectrum however, (the methyl region of which rather surprisingly shows only a singlet at 1.32 ppm.) no further spectroscopic or analytical data are given.

More recently the compound cis - $RuCl_2(PF_3)_2(PPh_3)_2$[146] has been synthesised by the reaction of $[RuCl_2(C_{10}H_{16})]_2$ ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl) with PF_3 and PPh_3 in dichloromethane solution. The structure was assigned as XXXVI by analogy with cis - $RuH_2(PF_3)_2(PPh_3)_2$ and this was confirmed by X-ray analysis.[147]



XXXVI

Finally, dimethyl(1-naphthyl)phosphine reacts with ruthenium trichloride (5:1 molar ratio) under reflux in 2-methoxyethanol to give the monomeric $RuCl_2L_3$ as deep red needles and the yellow $[Ru_2Cl_3L_6]^+$ cation, which may be isolated as the BPh_4^- salt.[148] The monomer is characterised by elemental analyses and molecular weight determination. It readily reacts with CO, MeCN and pyridine (L') to produce the corresponding $RuCl_2L_3L'$ complexes. The formation of the five coordinate species is presumably due to the large steric requirement of the dimethyl(1-naphthyl)phosphine ligand. However, although this is sufficient to favour the formation of the monomeric species, it is not so great as to prevent the formation of the triple-bridged species which contains three phosphines sharing one face of an octahedron.

2.2 Results and Discussion

Since their preparations were first reported[114] in 1966, $RuX_2(PPh_3)_{3or4}$ (X = Cl,Br) have proved to be extremely useful as source materials for the preparation of a series of complexes with carbon, sulphur, nitrogen and oxygen donor ligands.[118] Furthermore, they have proved invaluable as catalysts or catalyst precursors particularly in the field of olefin isomerisation,[149,150] hydrogenation[151] and oxidation.[152] $RuCl_2(PPh_3)_3$ has also been used in the dehydration of tertiary alcohols and in the racemisation and H/D exchange of secondary alcohols.[153,154] It also catalyses the alcoholysis of diarylsilanes,[155] the hydrogenation of oxygen to water[156] and promotes exchange of D_2 with -OH and -NH bonds.[157]

As has been already discussed, monomeric complexes of this formulation were generally unknown for the monotertiary phosphines of the type $PRPh_2$, PR_2Ph, PR_3 (R = alkyl) and therefore a general method of synthesis of these compounds was sought.

Compounds of the type RuX_2L_4 (X = Cl,Br: L = $P(OPh)_3$, $P(O\ tolyl)_3$, $P(O\ p\text{-}ClPh)_3$, $P(OCH_2CH_2Cl)_3$)[158] have been prepared by refluxing $RuX_2(PPh_3)_4$ with an excess of tertiary phosphite in either dichloromethane, ethanol or hexane. This technique was extended to various tertiary phosphines. However, as previously observed, the complexes which ruthenium forms with monotertiaryphosphines are extremely sensitive to the nature of the solvent and of the phosphine used.

Thus, the exchange reactions carried out with $RuX_2(PPh_3)_{3or4}$ (X = Cl,Br) and a sixfold excess of tertiary phosphine in dichloromethane or ethanolic solution resulted in the formation of the yellow $[Ru_2X_3L_6]X$ as the sole product. When however the same reactions were performed in hexane or light petroleum (b.p 60-80°C), neutral

ruthenium(II) complexes were isolated. The products proved dependent upon the nature of the phosphine ligand used. Thus when dimethylphenylphosphine or methyldiphenylphosphine was used, the complex isolated was of the type RuX_2L_4, whereas with ethyldiphenylphosphine the tris complex precipitated. However when L is diethylphenylphosphine or chlorodiphenylphosphine the neutral triple halide bridged dimers $[L_2XRuX_3RuL_3]$ are isolated.

Furthermore although the neutral complexes are quite stable in the solid state, the monomeric complexes RuX_2L_{3or4} in particular (L = PMe_2Ph, $PMePh_2$, $PEtPh_2$, PPh_3) all undergo facile rearrangement reactions in solution. As a result characterisation of these species and their rearrangement pathways proved impossible (with the exception of L = PMe_2Ph) by the conventional techniques of ^1H nmr, due both to the basic complexity of, and the very small chemical shift differences between, the resonances arising from the different species involved.

The infra-red spectra of the complexes in the region 4000 to 400 cm^{-1} show little variation between the different species for a given phosphine. However, use of far infra-red spectroscopy (400 - 150 cm^{-1}) enabled a more detailed study of the metal halide stretching frequencies which permitted terminal and bridging halides to be distinguised and thus provided valuable structural information. This region also proved useful as a "fingerprint" region for the identification of the complexes involved.

It was however, the use of variable temperature, Fourier Transform, proton noise decoupled ^{31}P nmr spectroscopy (because of the large chemical shift differences exhibited by the different phosphorus nuclei as compared to protons) that enabled these complexes to be characterised and their rearrangement reactions in solution to be studied in some detail.

a) L = PPh_3

Until recently the species present in solutions of $RuCl_2(PPh_3)_{3or4}$ have received little investigation despite the large amount of work devoted to the study of the related complex $RhCl(PPh_3)_3$.[82] In the original paper reporting the preparation and characterisation of these complexes,[114] molecular weight determinations (performed osmometrically in acetone) produced values of about one third of the expected value for $RuCl_2(PPh_3)_3$ and one half for the tetrakis complex. It was therefore suggested that extensive dissociation of these complexes must occur in solution. Very recently, the behaviour of these complexes in solution has been reinvestigated spectrophotometrically by James and Markham.[159]

They examined the dissociation of $RuCl_2(PPh_3)_3$ in both benzene and dimethylacetamide solutions. These studies performed under strictly anaerobic conditions showed that $RuCl_2(PPh_3)_4$ is completely dissociated in solution:

$$RuCl_2L_4 \rightleftharpoons RuCl_2L_3 + L \qquad (13)$$

and that in a 10^{-3}M benzene solution, $RuCl_2(PPh_3)_3$ is about 80% dissociated at 25° in the absence of added phosphine.

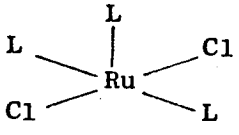
$$RuCl_2L_3 \rightleftharpoons RuCl_2L_2 + L \qquad (14)$$

Addition of excess triphenylphosphine to the solution of $RuCl_2(PPh_3)_3$ showed that the equilibrium in equation (14) was shifted to the left. The equilibrium constant at 298K for equation (14) was calculated as $2.7 \pm 0.5 \times 10^{-3}$M. Thermodynamic parameters were also calculated, ΔH^o being 17.6 ± 1 kJ mol^{-1}.

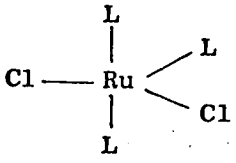
In an attempt to identify more directly the species present in

solution these compounds have been examined over a range of temperatures by proton noise decoupled ^{31}P nmr spectroscopy. The solutions studied were of a higher concentration (0.01M to 0.1M) than those examined by James and Markham (ca 10^{-3}M).

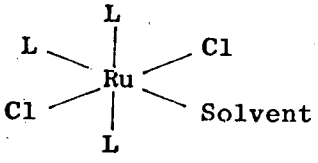
The spectrum of $RuCl_2(PPh_3)_3$ at 173K in a mixture of methylene-chloride and d^6 (deuterated) acetone (used as a lock signal) comprises a doublet (25.0 ppm) and a triplet (75.8 ppm) pattern (J_{PP} 30.3Hz) of relative intensity 2:1. This is consistent with the square pyramidal structure XXXVII for $RuCl_2(PPh_3)_3$ established by x-ray analysis (163) in which there is one apical and two trans- basal phosphines, the final coordination site being blocked by a phenyl ring. This spectrum is also consistent with a trigonal bipyramidal structure XXXVIII or a solvated octahedral structure XXXIX.



XXXVII



XXXVIII



XXXIX

However according to the symmetry rules for predicting molecular structures advanced by Pearson (160) and more recent work by Burdett (161) and Hoffmann, (162) the stable configuration for a 5 coordinate d^6 low spin system such as this, is one of C_{4V} symmetry i.e. square pyramidal.

Figure 1a shows the spectrum of a ca 0.1M solution of the complex in deoxygenated $CDCl_3$ at 200K. The spectrum consists mainly of the two broad signals at 25.0 and 75.0 ppm. due to the compound itself, but

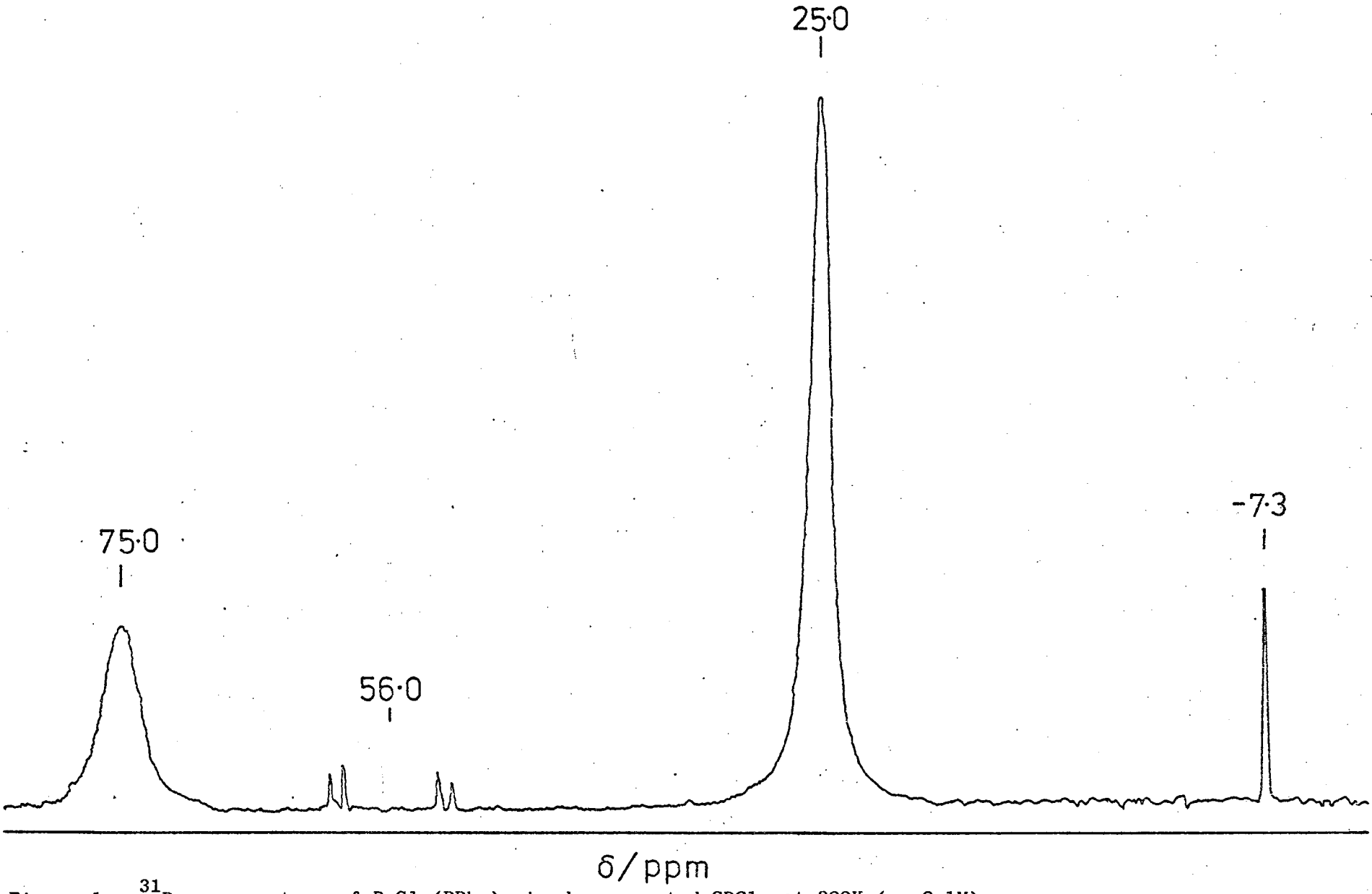


Figure 1a ^{31}P nmr spectrum of $RuCl_2(PPh_3)_3$ in deoxygenated $CDCl_3$ at 200K (ca 0.1M).

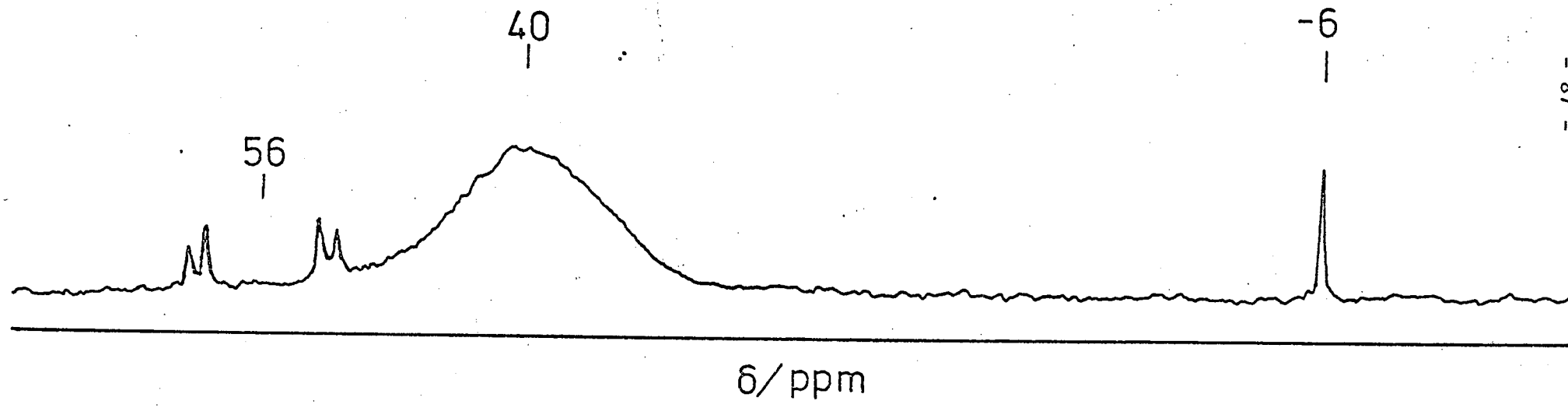


Figure 1b ^{31}P nmr spectrum of $RuCl_2(PPh_3)_3$ in deoxygenated $CDCl_3$ at ca 250K (ca 0.1M).

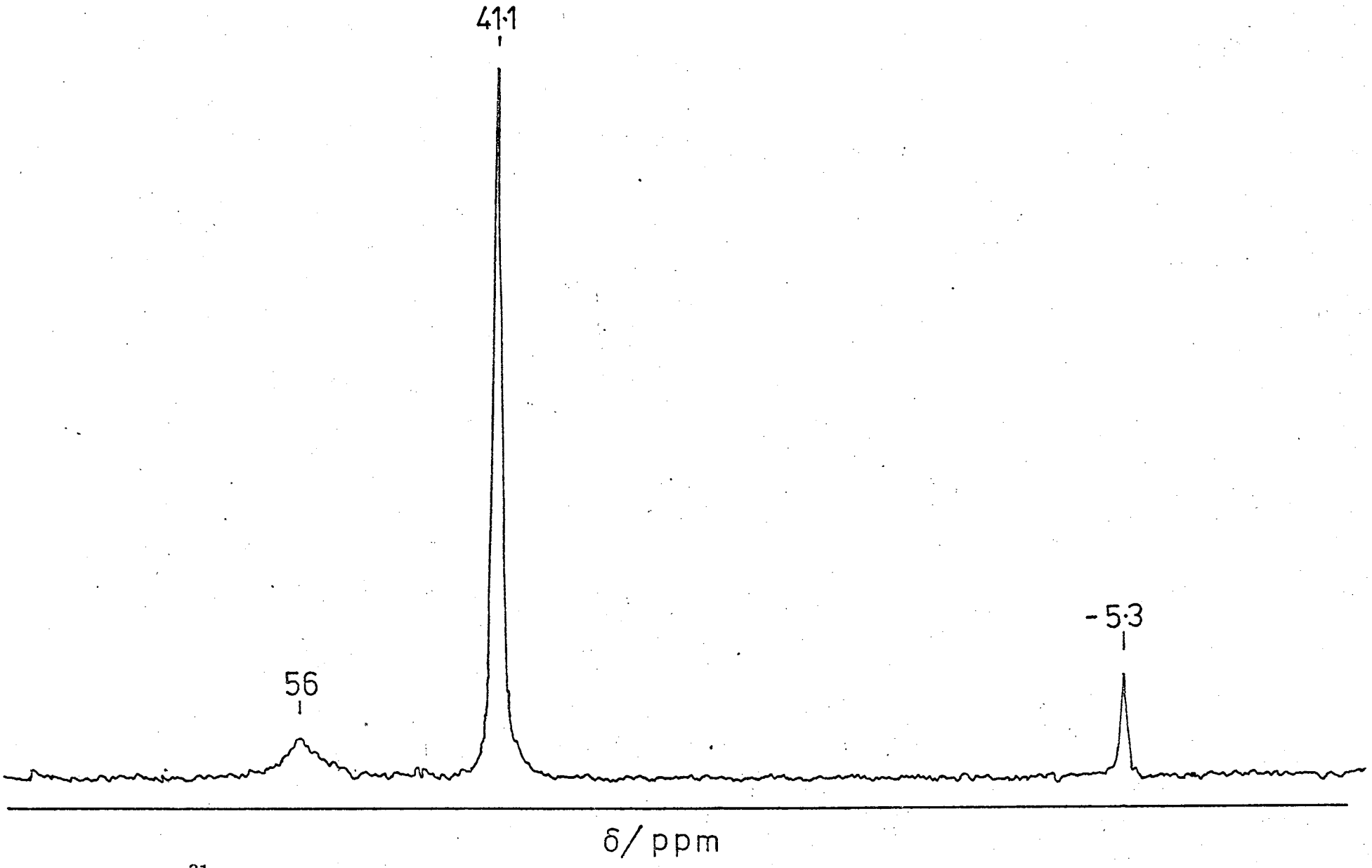


Figure 1c ^{31}P nmr spectrum of $RuCl_2(PPh_3)_3$ in deoxygenated $CDCl_3$ at ca 300K (ca 0.1M)

in addition there are some weak signals centred at 56.0 ppm. which comprise an AB pattern (Jpp=42Hz, $\delta p_1 p_2$=320Hz) and a small singlet at -7.3 ppm. (free PPh_3) which are of relative intensity 2:1.

The main signals broaden still further on raising the temperature and then coalesce (ca 250K) (fig. 1b) and finally give rise to a sharp singlet (> 290K) at 41.1 ppm. (fig. 1c). The smaller peaks broaden and coalesce at a slightly higher temperature (ca 290K) (fig. 1c). The free triphenylphosphine resonance remains sharp but shifts slightly to lower field (-7.3 ppm. at 200K to -5.3 ppm. at 308K). The spectrum shown in figure 1a is reproduced on lowering the temperature to 200K. These spectra indicate that in a 0.1M solution of $RuCl_2(PPh_3)_3$ dissociation is only slight (estimated 5%).

However at 220K the spectrum of a 0.01M solution of the complex in a mixture of toluene and d^6 benzene (used as a locking signal) shows that the AB pattern at 57.6 ppm. and the free triphenylphosphine resonance (-6.9 ppm.) are greatly increased in intensity relative to the $RuCl_2(PPh_3)_3$ signals (fig. 2). Further, on the addition of an excess of free triphenylphosphine the AB pattern disappears, indicating that the resonances arise from a dissociation product of $RuCl_2(PPh_3)_3$. It can be seen that in the more dilute solution considerable dissociation of the tris-phosphine complex occurs (ca 30%).

Whilst this work was in progress, similar results to these were reported by Caulton et al which are in excellent agreement with those described above.[70,164]

The AB resonance pattern is attributed to the dissociated complex "$RuCl_2(PPh_3)_2$". This complex is unlikely to be a monomeric species as, if it were of tetrahedral or square planar configuration, the ^{31}P nmr spectrum would be only a singlet and the other possibility of a cis-

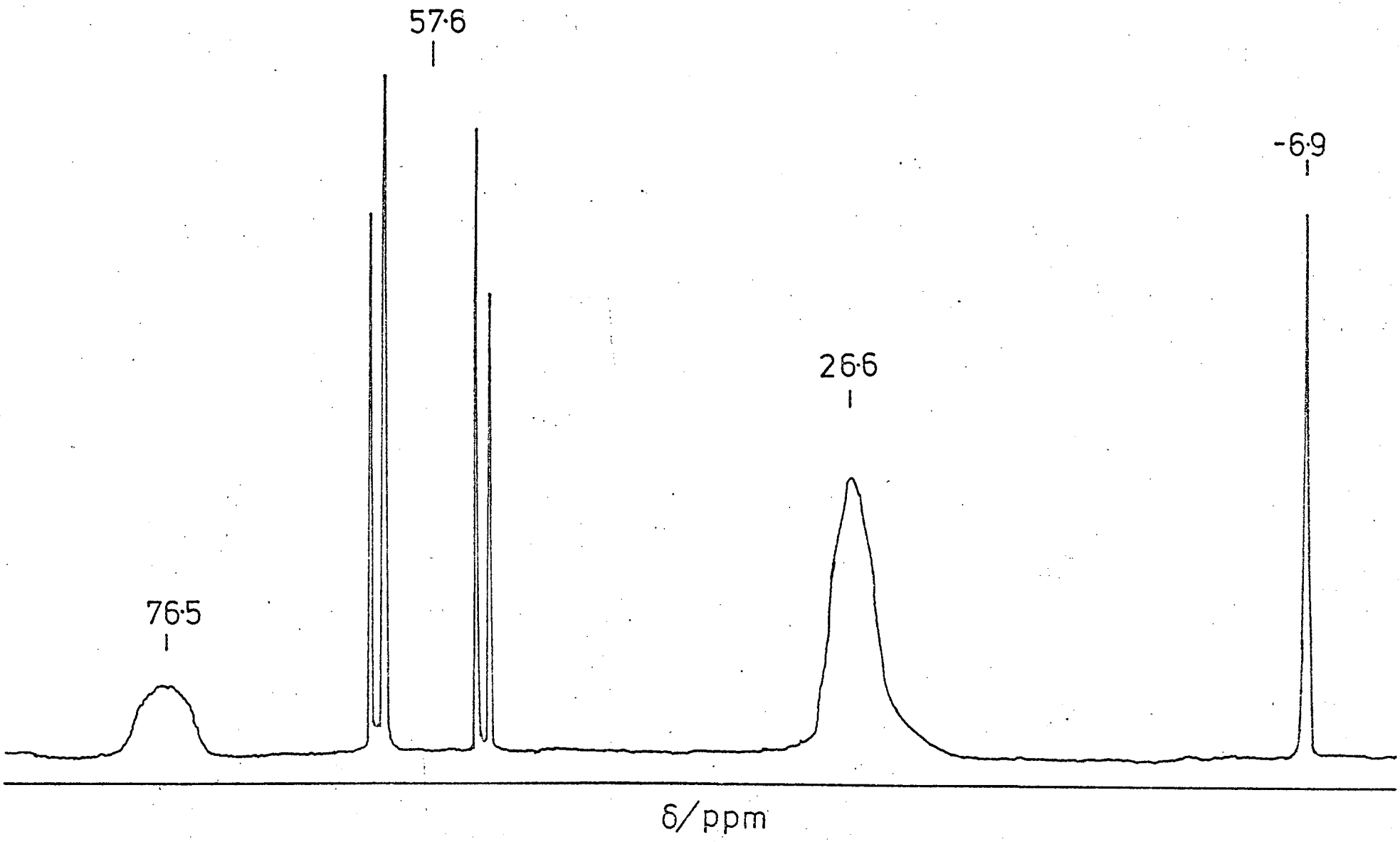
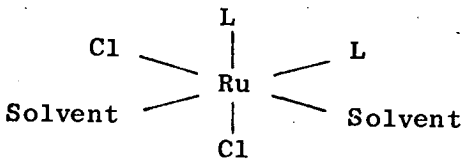


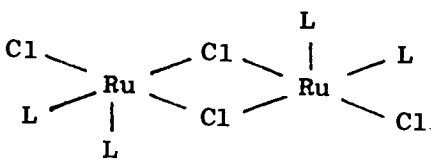
Figure 2 ^{31}P nmr spectrum of $RuCl_2(PPh_3)_3$ in deoxygenated toluene/benzene at 220K (ca 0.01M)

octahedral complex of the type $RuCl_2(PPh_3)_2(solvent)_2(XL)$ is very unlikely in such solvents as chloroform or toluene.



XL

The spectrum is however, consistent with a dimeric structure (XLI) in which two square pyramids share an edge by means of a double halide bridge.



XLI

The structural conclusions made about the dissociated species are in agreement with those of Caulton,[164]† and show that the dissociation mechanism for the ruthenium system is analogous to that established for the behaviour of $RhClL_3$ ($L = PPh_3$, $P(p\text{-tolyl})_3$) in solution:[82]

$$2RhClL_3 \rightleftharpoons [RhClL_2]_2 + 2L \qquad (15)$$

Earlier spectrophotometric studies[165] on this system (for $L = PPh_3$) were also erroneously interpreted in terms of an equilibrium analogous to (14) i.e.

$$RhClL_3 \rightleftharpoons RhClL_2 + L \qquad (16)$$

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†Very recent work by Cenini et al who have examined the ^{31}P nmr spectrum of a 0.05M solution of $RuCl_2(PPh_3)_3$ in $CH_2Cl_2/C_6D_5CD_3$ solution at 213K and ambient temperature observesno evidence for any dissociation.[166]

Thus on the basis of nmr evidence equilibrium (14) should be reformulated for $RuCl_2(PPh_3)_3$ as:-

$$2RuCl_2L_3 \rightleftharpoons [RuCl_2L_2]_2 + 2L \qquad (17)$$

James and Markham[159] had considered the possibility of (17) instead of (14) but had concluded that dimerisation would not be significant in 10^{-3}M solutions. However these ^{31}P nmr studies have shown that the same dissociation product is present at 0.1M and 0.01M concentrations and the spectral pattern is inconsistent with a monomeric structure. Furthermore, Caulton has recorded the ^{31}P nmr spectrum of a 7×10^{-4}M solution of $RuCl_2(PPh_3)_3$ in CH_2Cl_2 at 303K[70] and found no peaks other than those exhibited by the more concentrated solutions. Apart from the difference that there is a monomer/dimer dissociation as opposed to a monomer/monomer dissociation, the ^{31}P nmr and spectrophotometric results are in good agreement.

A lineshape analysis performed by Caulton and Hoffman on the spectrum of $RuCl_2(PPh_3)_3$, provides parameters which are consistent with the exchange process within the monomer itself being an intramolecular process. This would appear to be most likely as the resonance lineshapes appear to be concentration independent and intermolecular exchange between free and bound phosphine groups of either of the ruthenium complexes appears to be slow.

The determination of thermodynamic parameters for equation (17)[70] proved impracticable due to the insolubility of the black bis phosphine polymer which precipitates out at low temperatures. It is also interesting to note that the corresponding osmium complex $OsCl_2(PPh_3)_3$ does not exhibit any appreciable phosphine dissociation.[70]

Both spectrophotometric[159] and ^{31}P nmr evidence show that for $RuCl_2(PPh_3)_4$ equilibrium (13) lies completely to the right hand side. Thus

the ^{31}P nmr spectrum of the complex in a 0.1M solution at 153K in $CH_2Cl_2/(CD_3)_2CO$ solution (fig. 3) shows complete dissociation into $RuCl_2(PPh_3)_3$ and PPh_3. There is no evidence for $RuCl_2(PPh_3)_4$ in solution even upon the addition of a large excess of PPh_3 to the solution. The ^{31}P nmr spectrum at higher temperatures is identical to that of $RuCl_2(PPh_3)_3$ with the exception that there is no evidence for the AB pattern due to the dissociated species (as there is an excess of PPh_3 present, the dissociation is inhibited).

Tolman et al[63] have suggested that the tetrakis triphenylphosphine complex of nickel NiL_4 is best represented as $NiL_3.L$, with one phosphine simply trapped in the lattice. It would appear from the ^{31}P nmr data that the ruthenium complex should perhaps be considered as being of the same type. This observation would account for the similar colours of $RuCl_2(PPh_3)_3$ and $RuCl_2(PPh_3)_4$ and also for the variable analytical data found for the latter.

The observed ^{31}P nmr spectra of these complexes are different when air is admitted to the system. First, $RuCl_2(PPh_3)_3$ dissolves to a far greater extent and solutions of the complex (as observed when these were first reported[114]) rapidly turn green, compared with their orange-brown appearance under anaerobic conditions.

When exposed to the air for short periods only, the spectra are little different to those observed in the deoxygenated system, with the exception of the appearance of a sharp singlet at 29.4 ppm. due to triphenylphosphine oxide. At low temperatures (<220K) the growth of the $OPPh_3$ peak is slow indicating slow uptake of oxygen by the ruthenium system. However at ambient temperatures oxygen is absorbed rapidly. Concomitant with the rapid growth of the triphenylphosphine oxide resonance is the decrease in intensity of the signal at 41.2 ppm. indicating a breakdown of the $RuCl_2(PPh_3)_3$ complex.

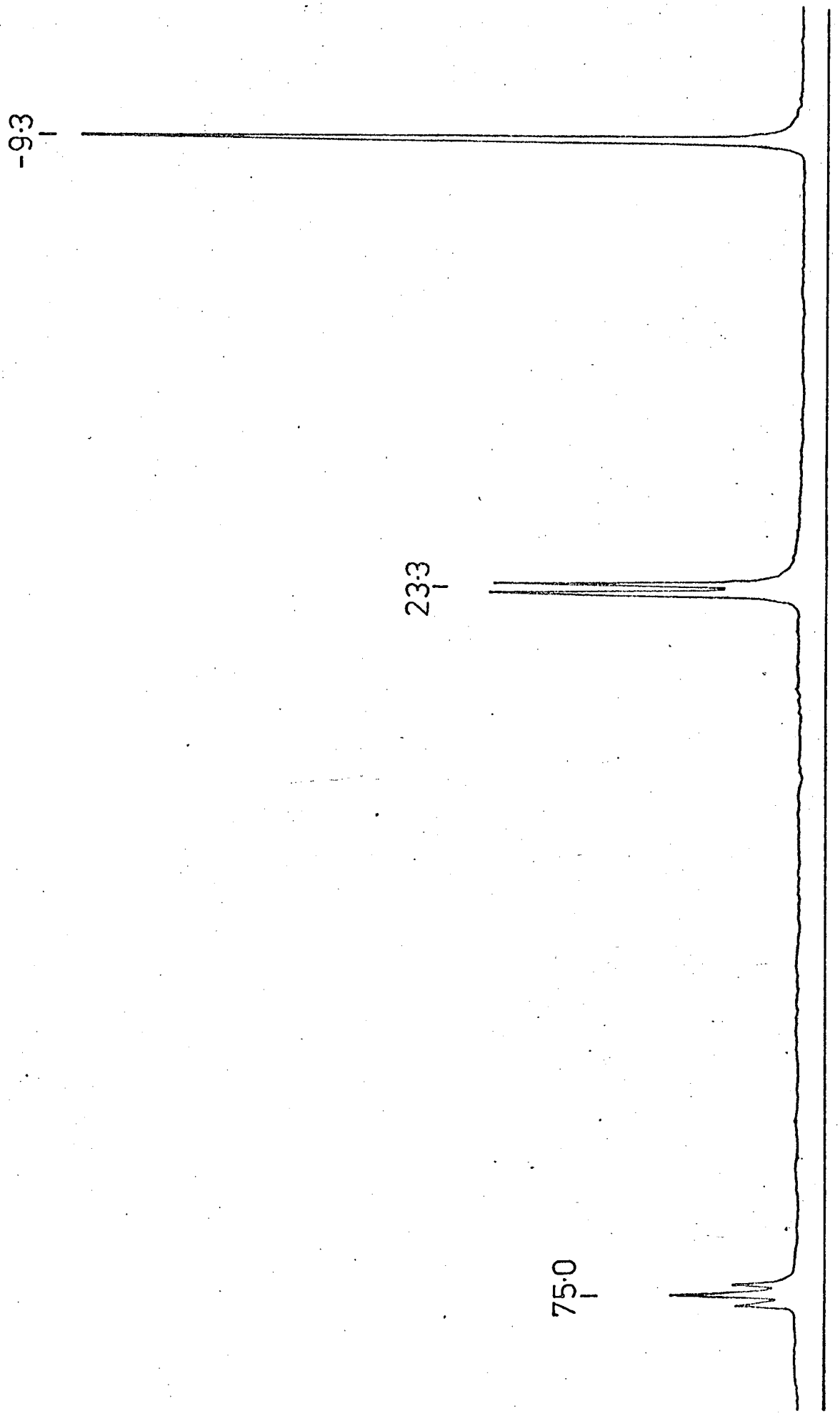
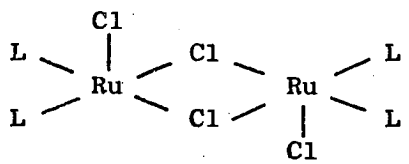


Figure 3 ^{31}P nmr spectrum of $RuCl_2(PPh_3)_4$ in $CH_2Cl_2/(CD_3)_2CO$ at ca 153K (ca 0.1M).

Addition of excess $OPPh_3$ to the system produces no shift in the position of the resonance at 29 ppm. indicating that this peak arises from free $OPPh_3$ and not from a ruthenium complex with the latter.† In addition an increase in intensity of the AB pattern is observed. Furthermore additional small peaks are observed in the spectrum; a weak singlet at 48.1 ppm. in $CDCl_3$ and, in $CH_2Cl_2/(CD_3)_2CO$ this weak singlet plus another more intense singlet at 38.8 ppm. are observed.

At ca 250K in the methylene chloride/acetone system, a large number of these additional peaks are observed (fig. 4). It is probable that these signals correspond to further types of dissociated species of the $RuCl_2(PPh_3)_3$ complex. However, it is only possible to speculate as to the nature of the species involved. The main possibilities would be a monomeric complex "$RuCl_2(PPh_3)_2$", the nature of which have been discussed earlier, or a dimer of the type shown (XLII).



XLII

Further possibilities could involve a ruthenium oxygen complex of the type $RuCl_2(O_2)(PPh_3)_2$ postulated by Cenini et al[152] and which has been isolated by Khan for the corresponding triphenylarsine system,[135] or a species involving coordinated $OPPh_3$ similar to the compound which Poddar et al have isolated for the $AsPh_3$ system.[168] As the signal at 38.8 ppm. is observed only in the acetone / methylene chloride spectrum it is tempting to speculate that this might correspond

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† Recently the formation of such a complex $[RuCl_2(OPPh_3)]_n$ has been proposed[166] as the product formed on exposing a solution of $RuCl_2(PPh_3)_3$ to oxygen.

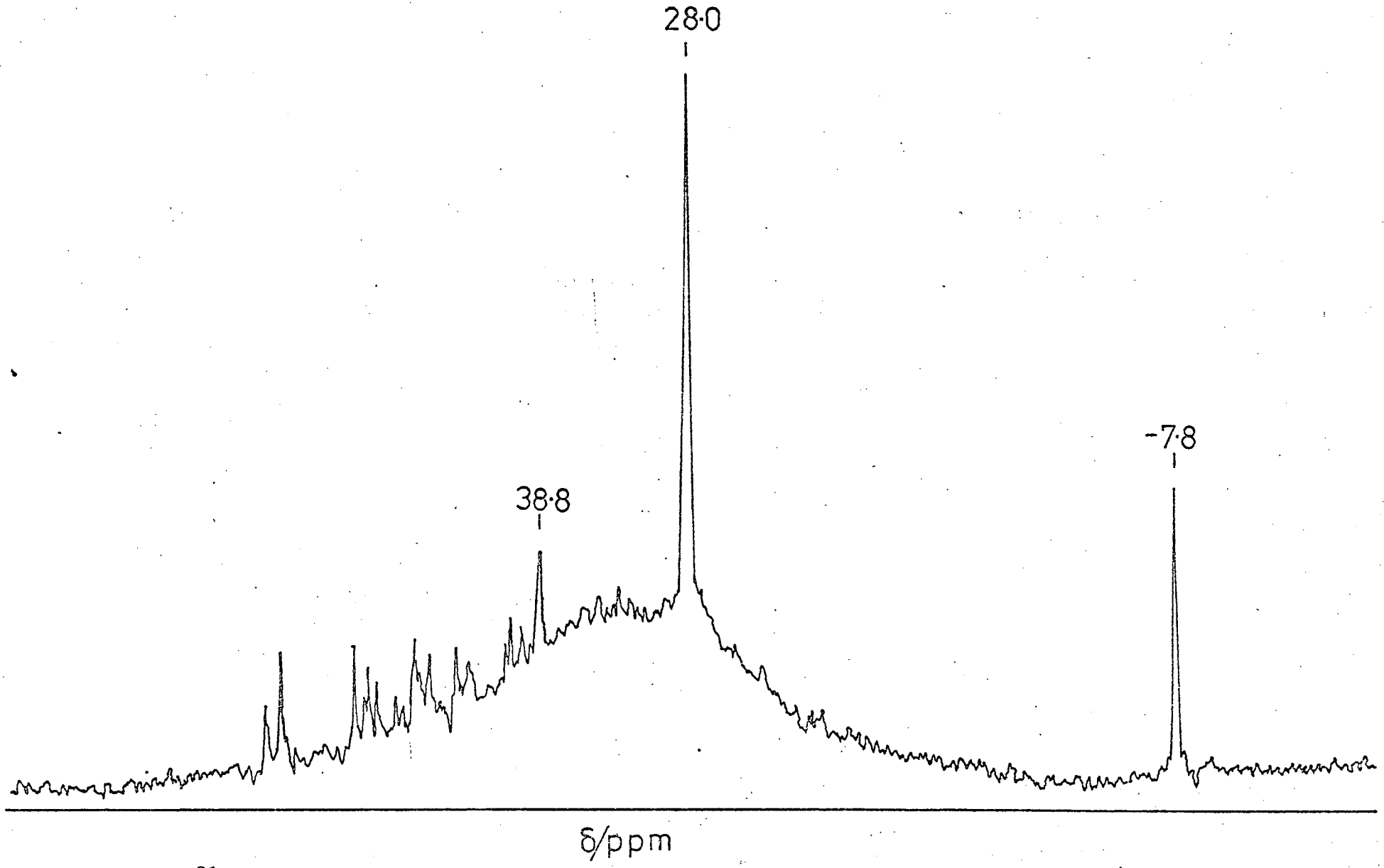


Figure 4 ^{31}P nmr spectrum of $RuCl_2(PPh_3)_3$ in $CH_2Cl_2/(CD_3)_2CO$ at ca 250K, in presence of oxygen.

to a complex of the type $[RuCl_2(PPh_3)_2 \text{ acetone}]_n$.

In their spectrophotometric examination of the $RuCl_2(PPh_3)_3$ system,[159] James and Markham observed that when solutions of the complex were exposed to air 1.5 to 1.6 moles of oxygen per mole of ruthenium were absorbed, which is consistent with the overall reaction:

$$RuCl_2(PPh_3)_3 + 1.5O_2 \rightarrow 3OPPh_3 + "RuCl_2" \qquad (18)$$

However it is interesting to note that the above reaction does not move completely to the right hand side as the signal due to $RuCl_2(PPh_3)_3$ at 41 ppm. could still be observed in the room temperature ^{31}P nmr spectrum of a solution of the complex which had been exposed to the air for 6 days.

When solutions of $RuCl_2(PPh_3)_4$ are exposed to the air, the rate at which triphenylphosphine oxide is formed is much less and the small extra resonances in the region 38 to 48 ppm. are not observed. This is also true of solutions of $RuCl_2(PPh_3)_3$ to which excess PPh_3 has been added. This is presumably because the presence of excess of triphenylphosphine shifts the equilibrium (17) to the left thus inhibiting the formation of the phosphine oxide. This observation whilst consistent with James and Markham's observation[159] that $RuCl_2(PPh_3)_3$ is virtually inactive as a catalyst for the oxidation of PPh_3 is contrary to the results obtained by Cenini et al,[152] in which the tris-complex was used to oxidise a tenfold excess of triphenylphosphine. The observation also implies that it may be the dissociated species "$RuCl_2(PPh_3)_2$" which is responsible for the observed oxidation and not $RuCl_2(PPh_3)_3$.

The alternative dissociation pathway available for $RuCl_2(PPh_3)_3$, which would be expected to be facilitated in more polar solvents, is loss of a chloride ion to produce ruthenium(II) cations (equations (19) and (20)).

Spectrophotometric and conductometric studies on N,N' - dimethylformamide solutions of $RuCl_2(PPh_3)_3$ indicated that these types of equilibria were important in polar solvents but no catonic complexes were isolated.(159)

$$RuCl_2L_3 \rightleftharpoons [RuClL_3]^+ + Cl^- \quad (19)$$

$$[RuClL_3]Cl \rightleftharpoons [RuClL_2]Cl + L \quad (20)$$

It was also noted that $RuCl_2(PPh_3)_3$ gave a pale yellow, air-stable solution in nitromethane,(114) which had a conductivity corresponding to that of a 1:1 electrolyte ($\Lambda_{0.001M} = 68\ \Omega^{-1}\ cm^2\ mole^{-1}$) but attempts to isolate solid complexes by solvent removal were unsuccessful.

However, when $RuCl_2(PPh_3)_3$ is shaken in CH_3NO_2, under nitrogen, in the presence of $NaBPh_4$ for several hours, then by evaporating most of the solvent a yellow-green oil is obtained. When this oil is extracted into ethanol and then most of the ethanol is evaporated, a pale yellow solid is isolated. Varying analytical data were obtained for this solid (see experimental section). However, the conductivity of the solid in dichloromethane solution ($\Lambda_{1.26g.l^{-1}} = 32.5\times10^{-6}\ \Omega^{-1}$) clearly indicates the presence of ionic species. Although the solutions of $RuCl_2(PPh_3)_3$ in nitromethane are air stable, solutions of the pale-yellow solid in less polar solvents rapidly change colour from yellow to green, implying decomposition.

The ^{31}P nmr spectrum of the solid in $CDCl_3$ solution (exposed to the air) at 213K shows an AB quartet centred at 46.2 ppm. (J_{pp} = 29.7Hz; δ_{AB} = 108.7Hz), a weak singlet at 50.1 ppm., weak bond resonances at ca 30 to 50 ppm. and a very strong singlet at 27.0 ppm ($OPPh_3$) (see fig. 5).

In the absence of air the singlet due to $OPPh_3$ (27 ppm), although

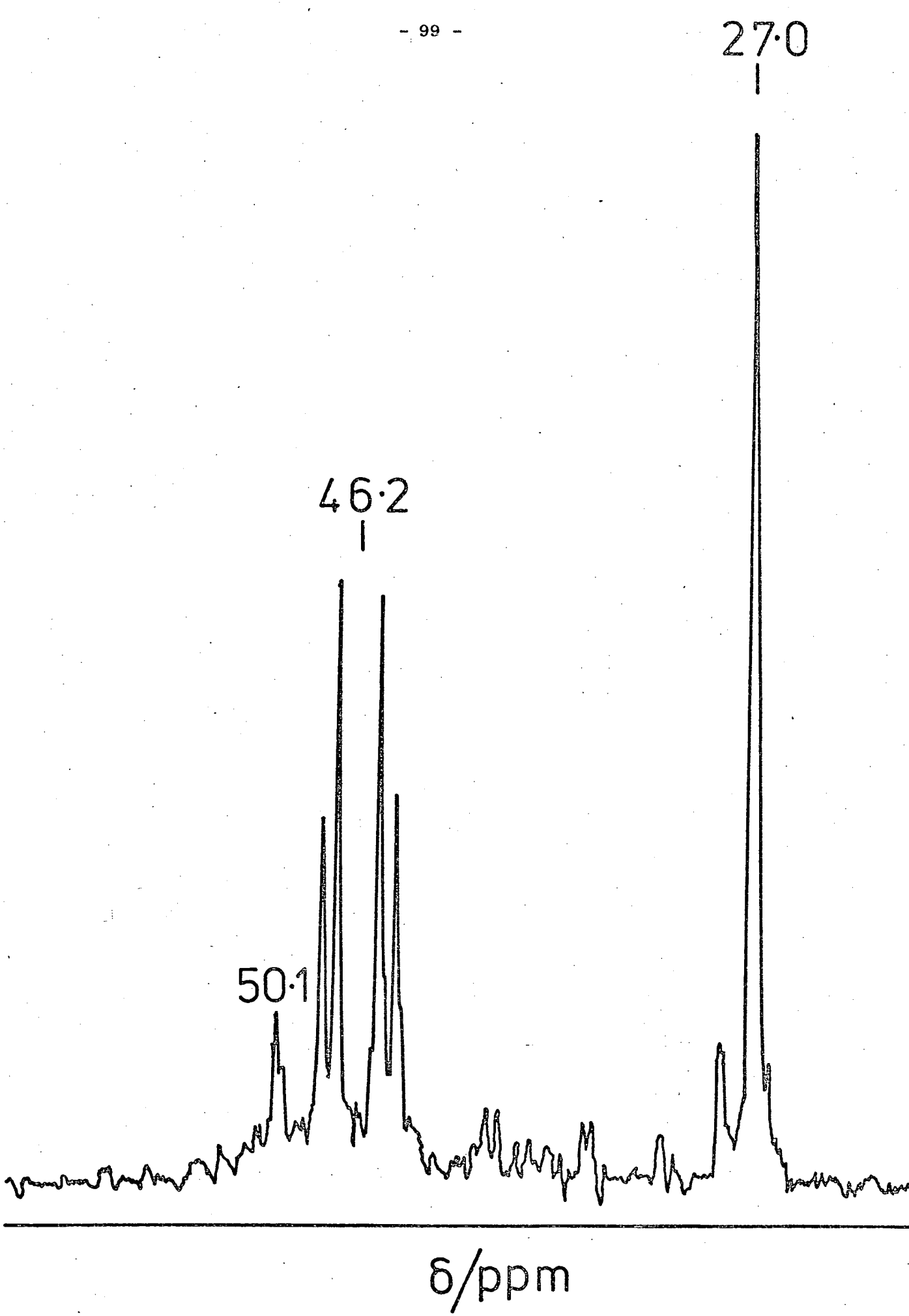
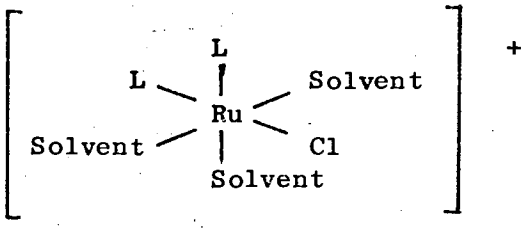


Figure 5 ^{31}P nmr spectrum in $CDCl_3$ at ca 213K of the product of the reaction between $RuCl_2(PPh_3)_3$, $NaBPh_4$ and CH_3NO_2.

less intense, may still be observed in the ^{31}P nmr spectrum in $CDCl_3$ at 213K, which also shows that the previously weak resonances at ca 30 to 50 ppm. are much more intense (although still broad) relative to the AB pattern.

By analogy with the spectrophotometric studies, it is tempting to speculate that the weak resonances ca 30 to 50 ppm. could be attributed to the presence of isomers of the complex $[RuCl(PPh_3)_3(CH_3NO_2)_2]^+$ which in the presence of air decompose with the formation of $OPPh_3$. Triphenylphosphine oxide must however, also be present in the reaction product as it is observed in the spectrum of the complex run in the absence of air. The AB quartet could then be attributed, tentatively, to the presence of the complex $[RuCl(PPh_3)_2(CH_3NO_2)_3]^+$ (XLII) which is consistent with the species postulated as a result of the spectrophotometric study[159] and also with the recent synthesis of compounds such as $[RuClL_2(MeCN)_3]PF_6$ (L = PPh_3, $PMePh_2$, PMe_2Ph) via $[RuCl(C_8H_{12})(MeCN)_3]PF_6$.[167]



(XLIII)

A preliminary investigation of the reaction between $RuCl_2(PPh_3)_3$ and $NaBPh_4$ in CH_3CN solution again indicated that a mixture of complexes was produced. These complexes decompose in the solid state over a period of hours and more rapidly in solution in less polar or non coordinating solvents.

The ^{31}P nmr spectrum of the product in $CDCl_3$ at 223K shows an AB quartet centred at 42.4 ppm. (J_{PP} = 27.5Hz; δ_{AB} = 152.5Hz) 2 singlets

49.6 and 37.4 and a singlet at 26.9 ($OPPh_3$).

Due to the complexity of the spectra obtained (particularly in CH_3NO_2 solution), the instability of the complexes and the difficulties encountered in attempts to separate the products (chromatography proved impossible due to poor separation and to decomposition) these systems were not investigated further.†

b) L = $PEtPh_2$

When $RuCl_2(PPh_3)_4$ was refluxed with excess ethyldiphenylphosphine in degassed hexane under nitrogen for ca 18 hours, green crystals were deposited which analysed closely for the empirical formula $RuCl_2(PEtPh_2)_3$. Likewise, reaction with $RuBr_2(PPh_3)_4$ gave the green $RuBr_2(PEtPh_2)_3$.‡

Prolonged reflux of $RuCl_2(PPh_3)_4$ with an excess of $PEtPh_2$ in ethanol or dichloromethane gave the lemon-yellow ionic dimer $[Ru_2Cl_3(PEtPh_2)_6]Cl$ (XXXV).

Comparison of the far infra-red spectra of these compounds clearly showed that the green complex contained no traces of the ionic dimer (see table 2:1) and that the position of νRu-Cl (327 cm^{-1}) was similar to that found for $RuCl_2(PPh_3)_3$ (315 cm^{-1}) which is consistent with a structure of type (XXXVII).

Although the ^1H nmr spectrum of this compound (which reveals two broad multiplets (7.3δ and 6.9δ) in the phenyl region and two very broad resonances (2.5δ and 0.6δ) in the ethyl region) was of no use in verifying this structure, confirmation was readily obtained from ^{31}P nmr studies.

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† The very recent synthesis of $[RuH(PPh_3)_3(CH_3CN)_2]BF_4$ may prove helpful in further investigations of these reactions.(71)

‡ See page 184

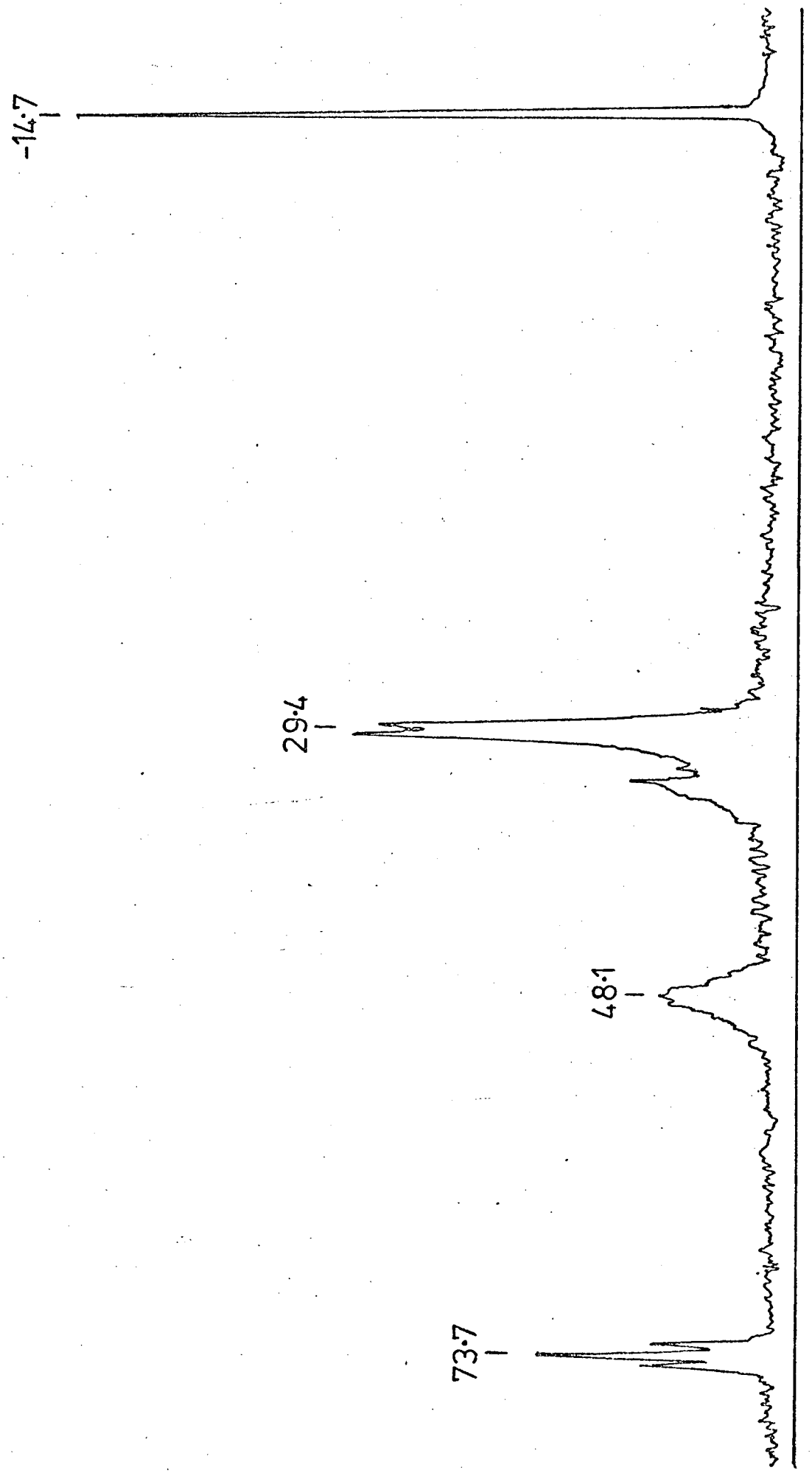


Figure 6 ^{31}P nmr spectrum of $RuCl_2(PEtPh_2)_3$ in $CH_2Cl_2/(CD_3)_2CO$ at ca 195K.

If the green complex is dissolved in degassed $CDCl_3$ at ca 225K, the ^{31}P nmr spectrum at this temperature consists of two strong signals at 30.4 and 73.3 ppm. (relative intensity 2:1) which in $CH_2Cl_2/(CD_3)_2CO$ solution at 195K are resolved into a doublet and triplet pattern respectively (J_{pp} = 30.0Hz). In addition, there is a very weak broad resonance centred at ca 47 ppm., together with a very sharp peak at ca -13 ppm. assigned to free $PEtPh_2$.

Thus by analogy with the triphenylphosphine studies, this clearly shows that the green complex has the same structure in solution as $RuCl_2(PPh_3)_3$ and that there is very little dissociation of the type shown in either equation (14) or (17) at this temperature and concentration (ca 0.01M).

However, if $RuCl_2(PEtPh_2)_3$ is first dissolved at room temperature and then cooled to lower temperature for examination, the observed ^{31}P nmr spectra are more complicated. Thus, at 195K in $CH_2Cl_2/(CD_3)_2CO$ solution, in addition to the peaks at 29.4 ppm. and 73.7 ppm. (due to the tris complex), the spectrum consists of a broad resonance at 48.1 ppm., a strong sharp resonance at -14.7 ppm. (free $PEtPh_2$) and a broad asymmetric resonance between 31 and 34 ppm. (see fig. 6).

On raising the temperature, the triplet and doublet resonances (29.4 and 73.7 ppm.) lose their fine structure, start to broaden and also become progressively weaker with respect to the other peaks, so that by ca 250K, there is apparently very little $RuCl_2(PEtPh_2)_3$ remaining. At the same time, the peak at 48.1 ppm. becomes sharper and more intense, and it can then be seen that there is a very weak resonance on the high field side of this sharp singlet (at ca 47 ppm): figs. 7a,b, and 8.

The free phosphine resonance also increases in intensity and shifts slightly to lower field. The broad resonance between 34 and

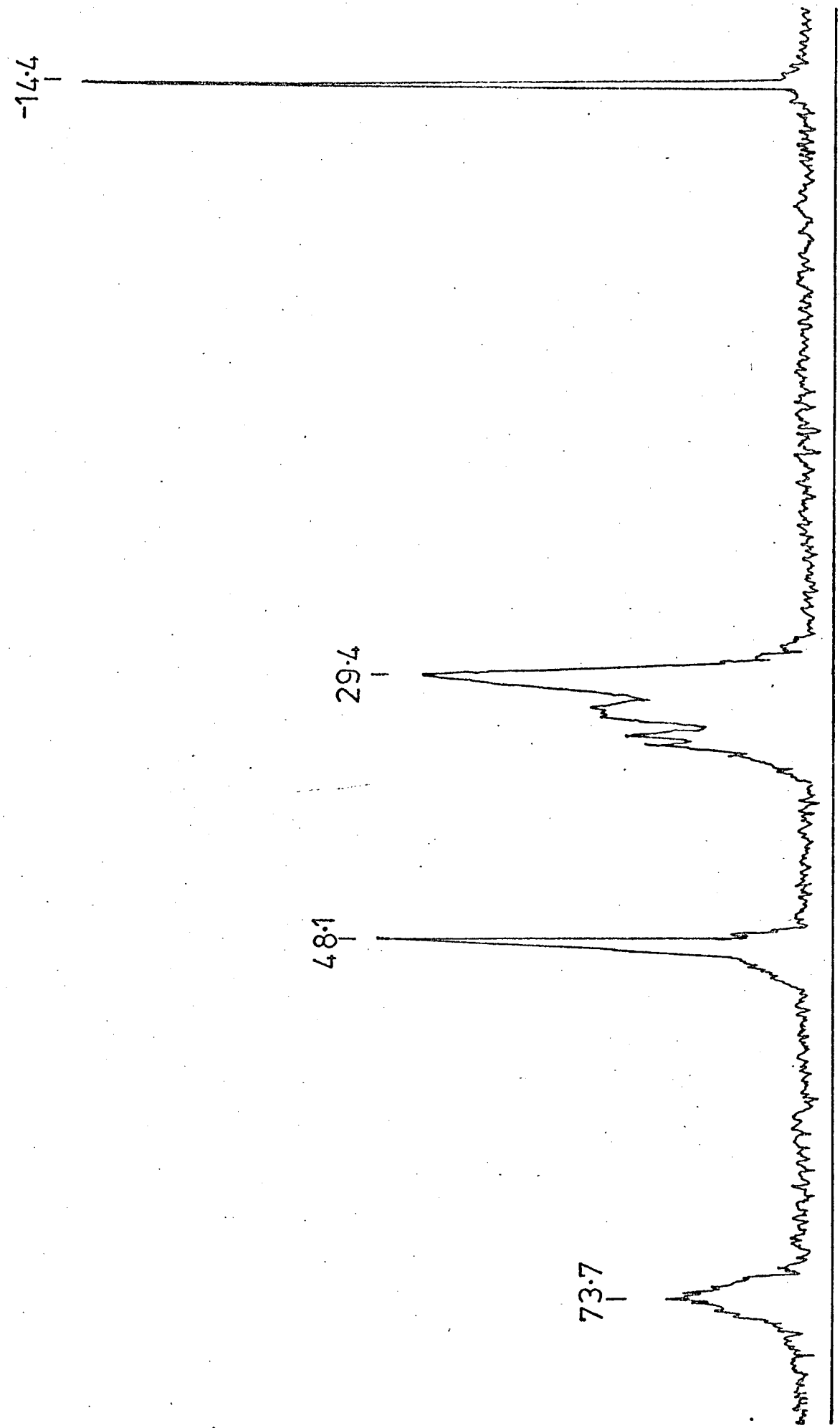


Figure 7a ^{31}P nmr spectrum of $RuCl_2(PEtPh_2)_3$ in $CH_2Cl_2/(CD_3)_2CO$ at ca 215K.

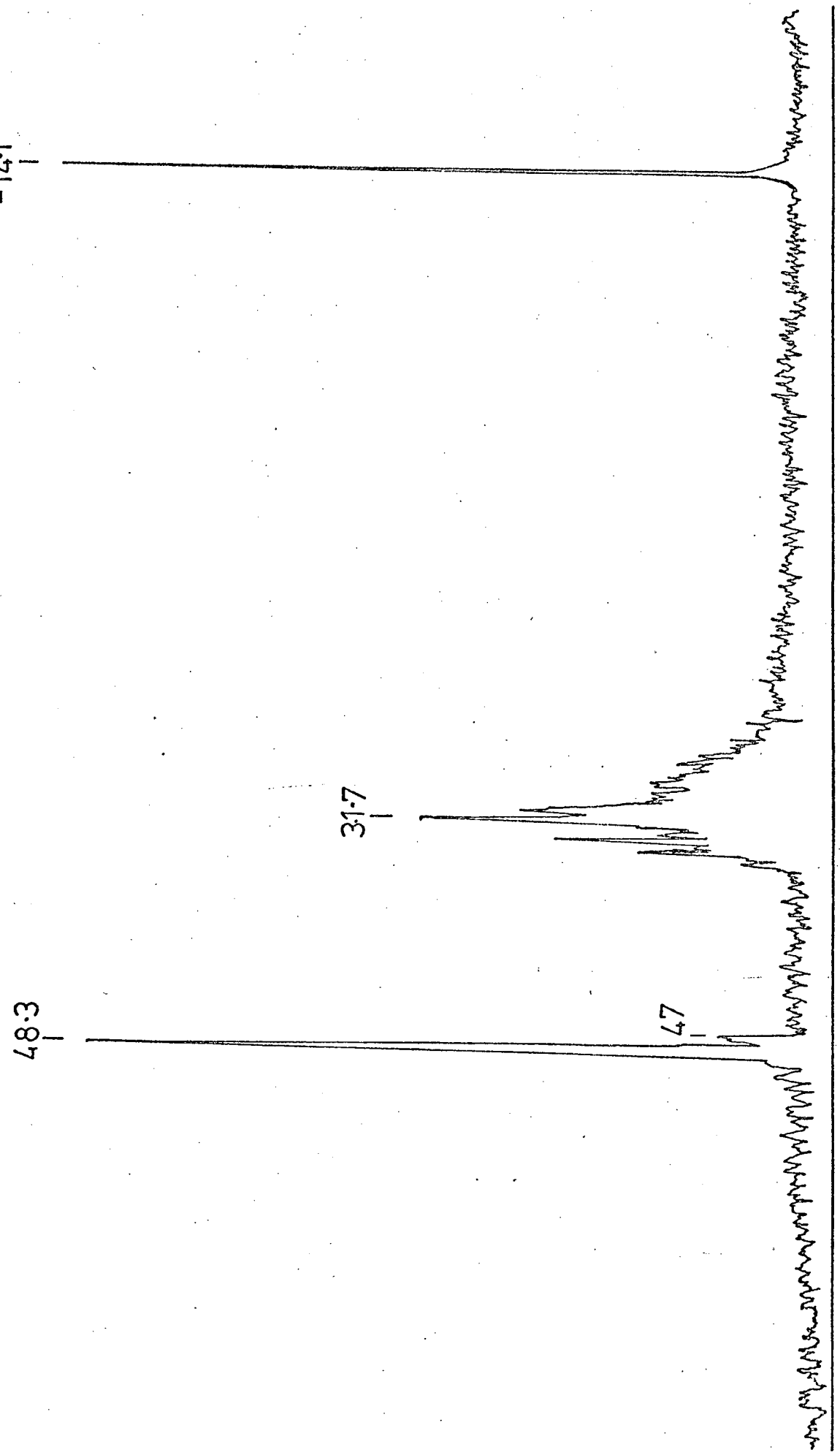


Figure 7b ^{31}P nmr spectrum of $RuCl_2(PEtPh_2)_3$ in $CH_2Cl_2/(CD_3)_2CO$ at ca 235K.

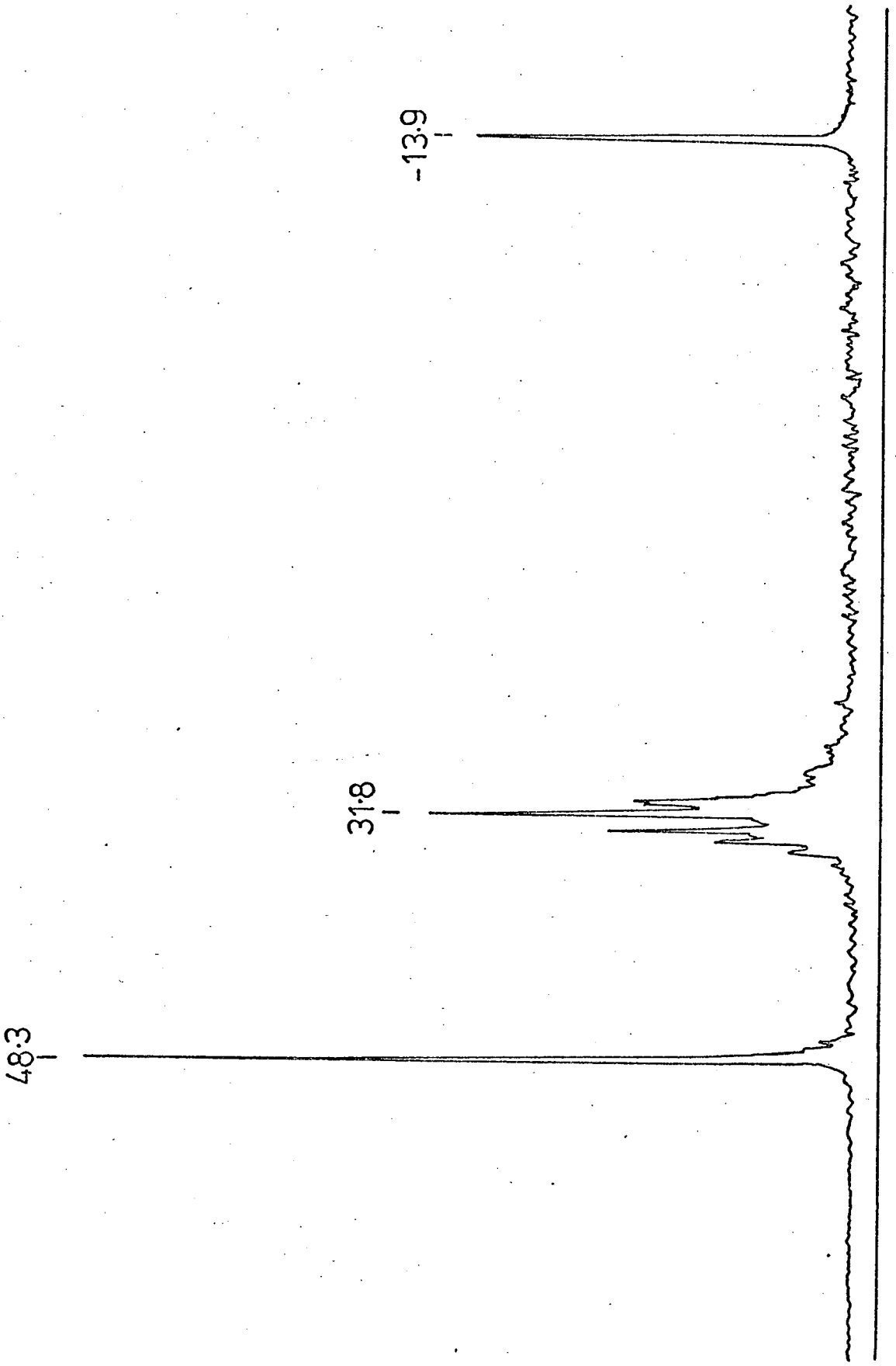


Figure 8 ^{31}P nmr spectrum of $RuCl_2(PEtPh_2)_3$ in $CH_2Cl_2/(CD_3)_2CO$ at ca 250K.

31 ppm both grows in intensity and becomes much sharper so that by ca 250K, it exhibits an unmistakable AB_2 pattern (fig. 8) [A, 33.7 ppm., B, 31.5 ppm.; δ_{AB} 91.0Hz; J_{AB} 27.3Hz]. Above 250K, a broad peak appears at ca 43 ppm. which corresponds to the averaged position of the two resonances of monomeric $RuCl_2(PEtPh_2)_3$ (cf $RuCl_2(PPh_3)_3$ 41.1 ppm.). All the other resonances are slightly decreased in intensity and the AB_2 resonance pattern starts to broaden (fig. 9a).

At 293K, the resonance at 43.0 ppm. has sharpened considerably and the AB_2 set has collapsed to a broad singlet at 32.0 ppm. with a strong shoulder at 33.0 ppm.; whereas, at 308K, there is a strong singlet at 32.6 ppm. and a weak shoulder at 32.1 ppm. The other peaks are little different except that the $PEtPh_2$ resonance (now at -12.3 ppm.) is broader and weaker than at lower temperatures (figs. 9b, 9c).

Finally, if this solution is left for three hours at 308K and then recooled to ca 213K (fig. 10), the spectrum is very similar to that observed earlier at this temperature (fig. 7a) except that, the resonances due to $RuCl_2(PEtPh_2)_3$ and free $PEtPh_2$ are much weaker on recooling and the various signals between 31 and 34 ppm. are comparable in position and intensity with those shown in fig. 7a except that the peak at 32.8 ppm (a weak shoulder in fig. 7a is now the strongest resonance in this part of the spectrum.

The same ^{31}P nmr spectra are observed for $RuCl_2(PEtPh_2)_3$ in $C_6D_6/C_6H_5CH_3$ solution except that all the resonances are shifted ca 2 ppm. to low field and that at 308K, there is only one broadened peak at 34.3 ppm. This indicates that with the exception of the complex which forms irreversibly in methylene chloride/acetone (at ca 32 ppm) and which is absent in benzene, all of the other resonances probably arise from non-ionic species.

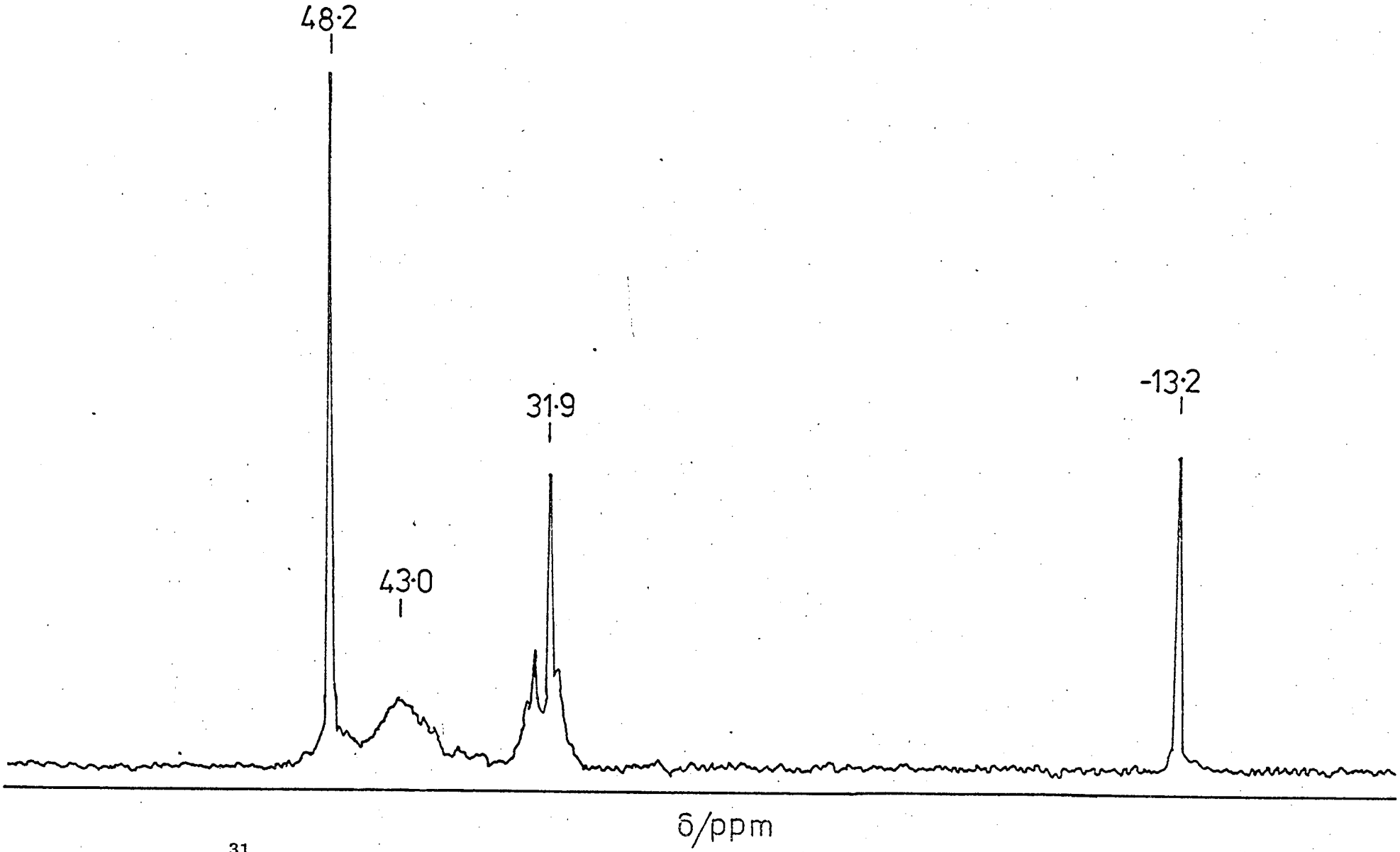


Figure 9a ^{31}P nmr spectrum of $RuCl_2(PEtPh_2)_3$ in $CH_2Cl_2/(CD_3)_2CO$ at ca 273K.

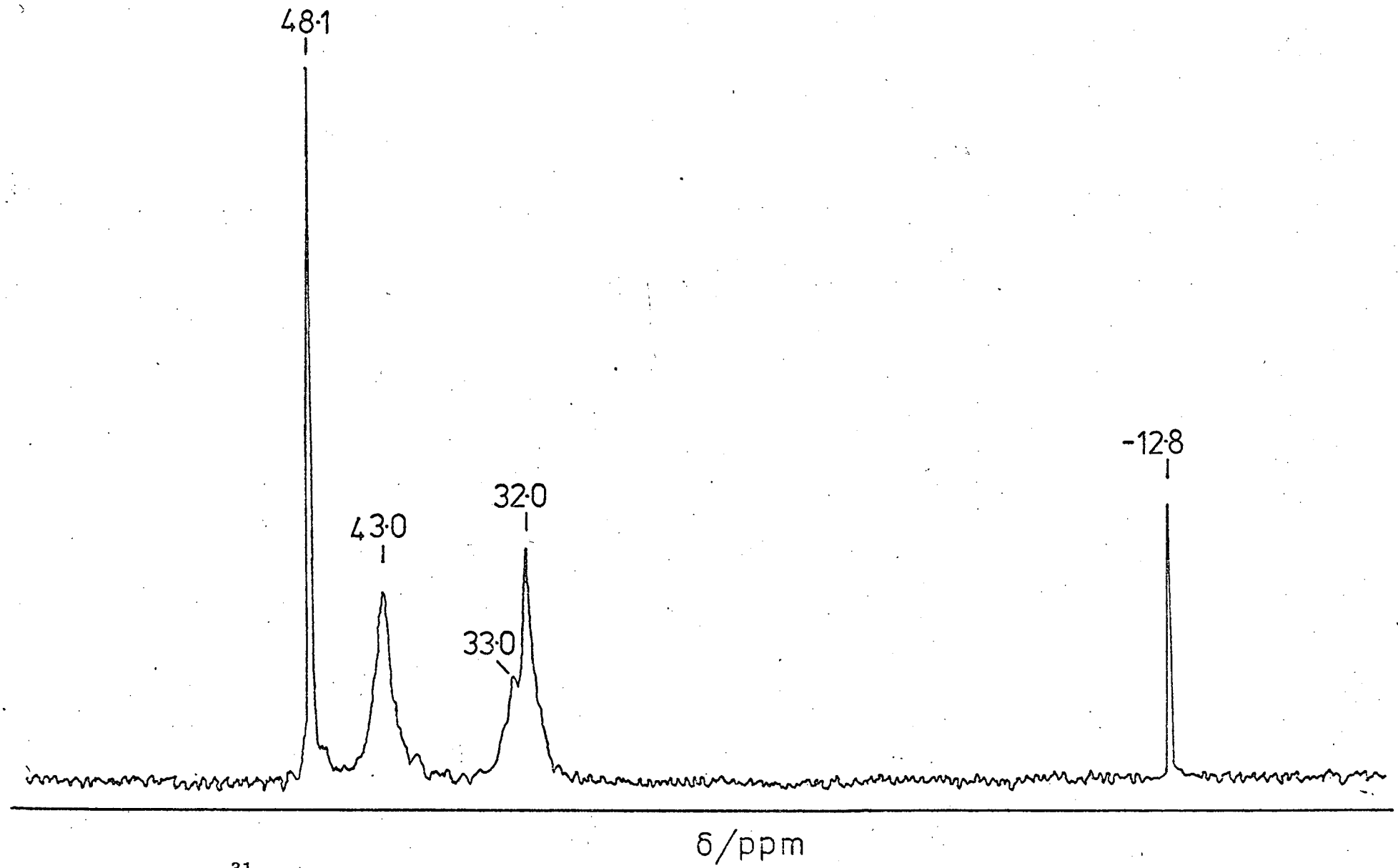


Figure 9b ^{31}P nmr spectrum of $RuCl_2(PEtPh_2)_3$ in $CH_2Cl_2/(CD_3)_2CO$ at ca 293K.

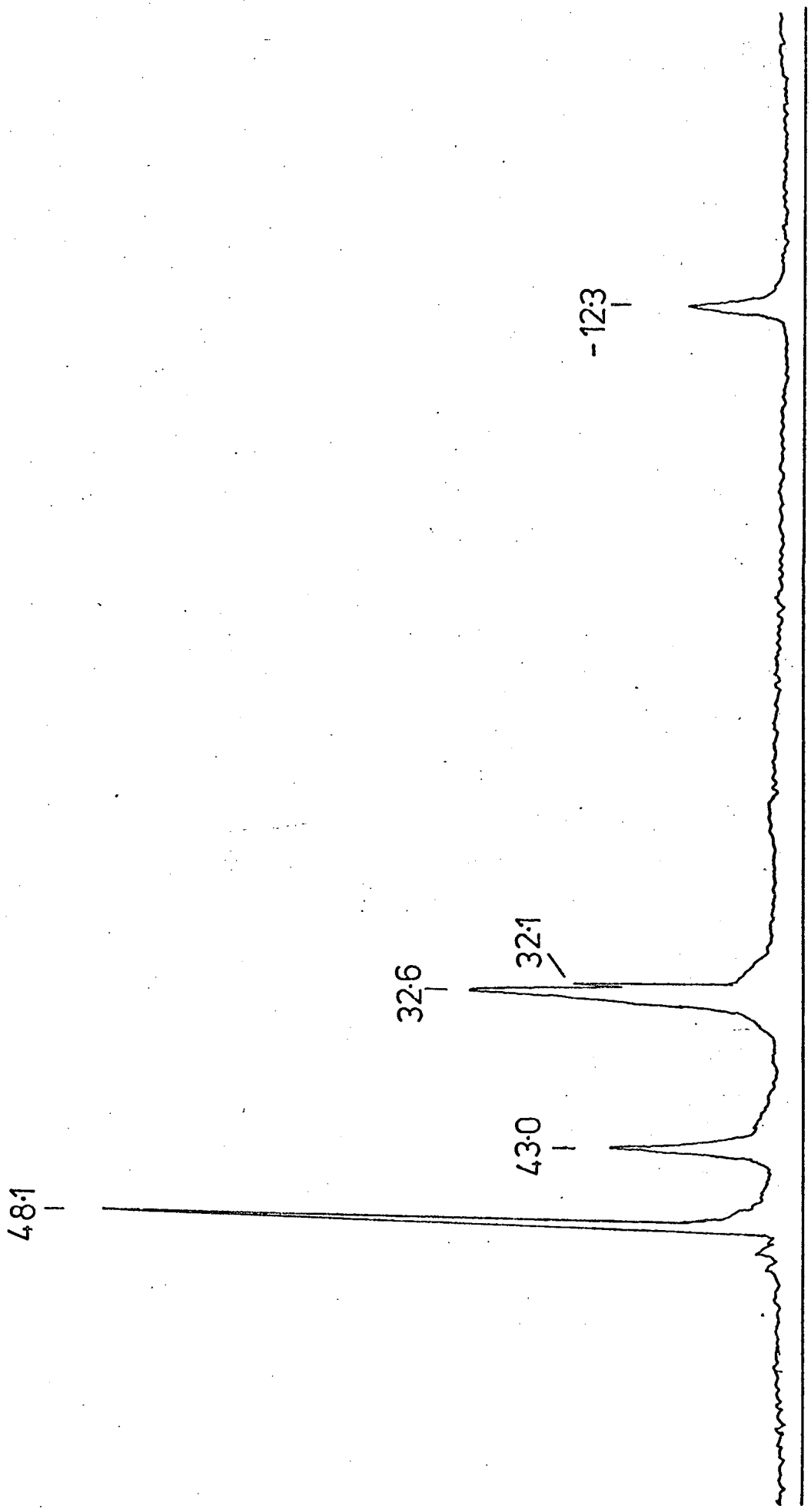


Figure 9c ^{31}P nmr spectrum of $RuCl_2(PEtPh_2)_3$ in $CH_2Cl_2/(CD_3)_2CO$ at ca 308K.

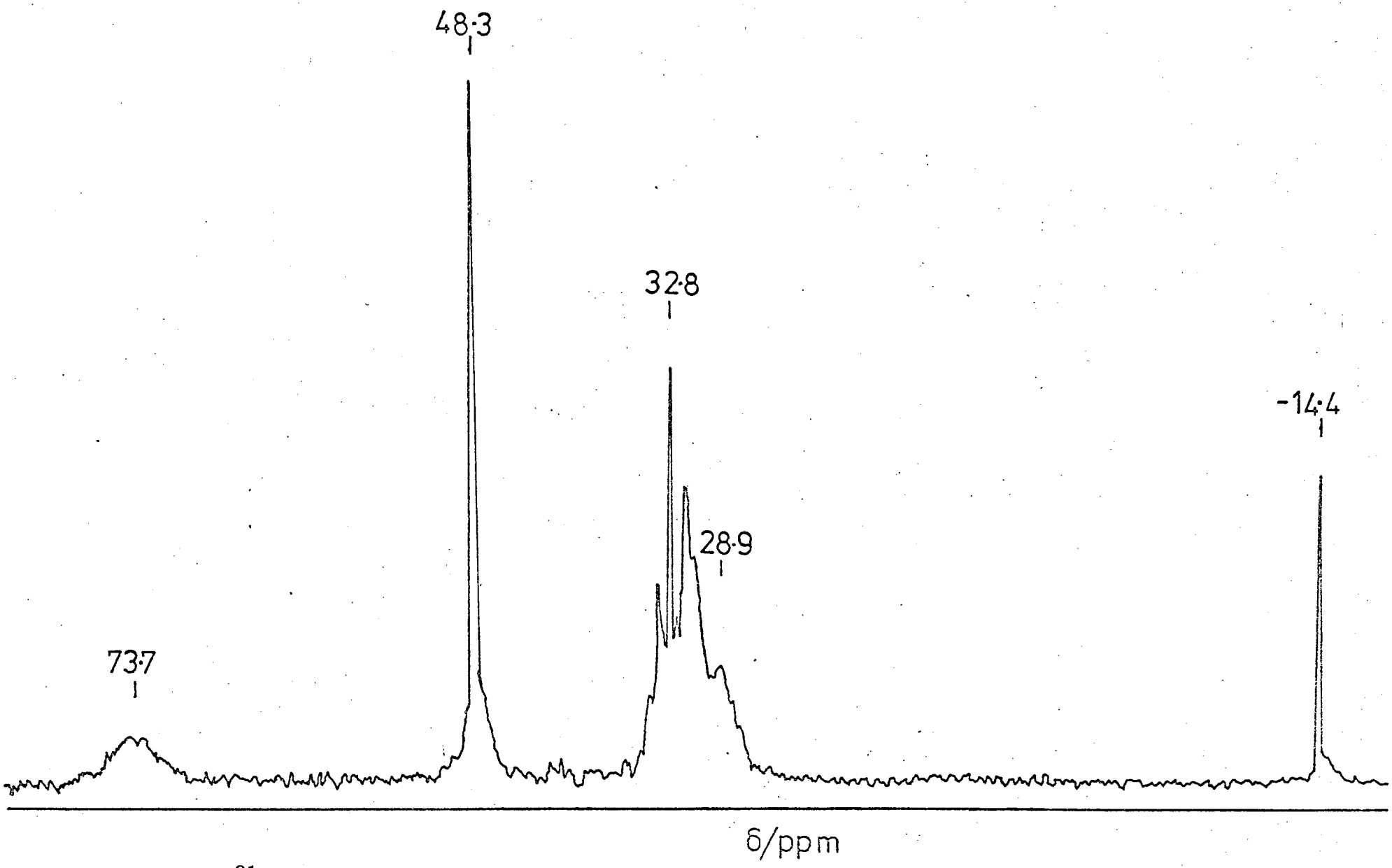
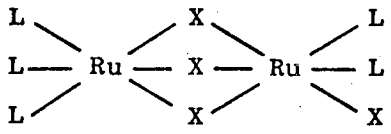


Figure 10 ^{31}P nmr spectrum of $RuCl_2(PEtPh_2)_3$ in $CH_2Cl_2/(CD_3)_2CO$ at ca 213K - sample recooled after 3h. at 308K.

Before discussing this system further it is necessary to consider three other experimental observations. First, the ^{31}P nmr spectrum of $[Ru_2Cl_3(PEtPh_2)_6]Cl$ (XXXV) (made by refluxing "$RuCl_3 3H_2O$" and excess $PEtPh_2$ in aqueous ethanol[128]) in $CDCl_3$ at 308K consists of a sharp singlet at 32.7 ppm. Furthermore, this compound does not undergo further reaction under the experimental conditions present in this study

Next, if $RuCl_2(PEtPh_2)_3$ is dissolved in CH_2Cl_2 at room temperature, the solvent removed from the green solution under vacuo and light petroleum (bp 60-80°C) added to the sticky residue, most of the material dissolves giving an orange-brown solution and a green residue ($RuCl_2(PEtPh_2)_3$ is <u>initially</u> completely <u>insoluble</u> in light petroleum)

Removal of solvent then gives an orange-brown solid whose ^{31}P nmr spectrum at 260K in C_6D_6/hexane consists of a sharp singlet at 50.4 ppm. and an AB_2 pattern between 33 and 36 ppm (relative intensity 2:3). This AB_2 pattern has identical parameters to that shown in fig. 8 (except for the low field shift of <u>ca</u> 2 ppm.). The orange-brown solid analyses for $Ru_2Cl_4(PEtPh_2)_5$ (XLIV) and further support for this



(XLIV)

formulation comes from molecular weight measurements in benzene.

The far infra-red spectrum shows the presence of both terminal (321 cm^{-1}) and bridging (260 cm^{-1}) νRu-Cl vibrations.

Finally, if $RuCl_2(PEtPh_2)_3$ is refluxed with excess $PEtPh_2$ in ethanol for three hours, a yellow conducting solution is formed which gives a yellow solid on solvent removal. The ^{31}P nmr spectrum of this material (which analysed closely for "$RuCl_2(PEtPh_2)_3$"), when dissolved

in $CDCl_3$ at 220K (fig. 11) consists of an AB_2 pattern which is superimposed on a sharp strong singlet at 33.1 ppm. ($[Ru_2Cl_3(PEtPh_2)_6]Cl$).

However, the AB_2 pattern of resonances has a different set of parameters from $Ru_2Cl_4(PEtPh_2)_5$, namely, A, 31.0 ppm.; B, 34.1 ppm.; δ_{AB}, 126.8Hz, J_{AB} 63.4Hz. Similarly reaction of $RuCl_2(PPh_3)_4$ with excess $PEtPh_2$ in refluxing ethanol for short periods gives a yellow solid with the same ^{31}P nmr spectrum in $CDCl_3$ at 210K as that shown in fig. 11.

On raising the temperature to 308K, the spectrum shows a very strong peak at 32.7 ppm. ($[Ru_2Cl_3(PEtPh_2)_6]Cl$), a weak peak at 43.1 ppm. ($RuCl_2(PEtPh_2)_3$, monomer), weak peaks at 48.5 and 32.1 ppm. (Ru_2Cl_4-$(PEtPh_2)_5$), -11.0 ppm. (free $PEtPh_2$) and a very weak AB_2 pattern compared to that observed at 210K. Thus it would appear the species giving rise to this AB_2 pattern is only stabilised at low temperature or in the presence of excess $PEtPh_2$. On raising the temperature in the absence of free $PEtPh_2$, it rearranges to form $RuCl_2(PEtPh_2)_3$, $[Ru_2Cl_3(PEtPh_2)_6]Cl$, $Ru_2Cl_4(PEtPh_2)_5$ and free $PEtPh_2$.

A complete rationalisation of all of these experimental observations could be provided by the rearrangement mechanism shown in scheme 2.1. Thus, it can be argued that for L = $PEtPh_2$ the dissociative pathway (i) (i.e. a dissociation of the type shown in equations (14) and (17) is of minor importance in that only a small amount of the dissociation product $[RuCl_2L_2]_n$ (resonance at 47 ppm.) is observed under all experimental conditions and the decomposition to produce phosphine oxide as shown in equation (18), which was of paramount importance in the triphenylphosphine system appear to be of little or no importance here.

The formation of $[Ru_2X_3L_6]X$ and $Ru_2X_4L_5$ (X = Cl, L = $PEtPh_2$) can be explained in terms of an associative process followed by intramolecular

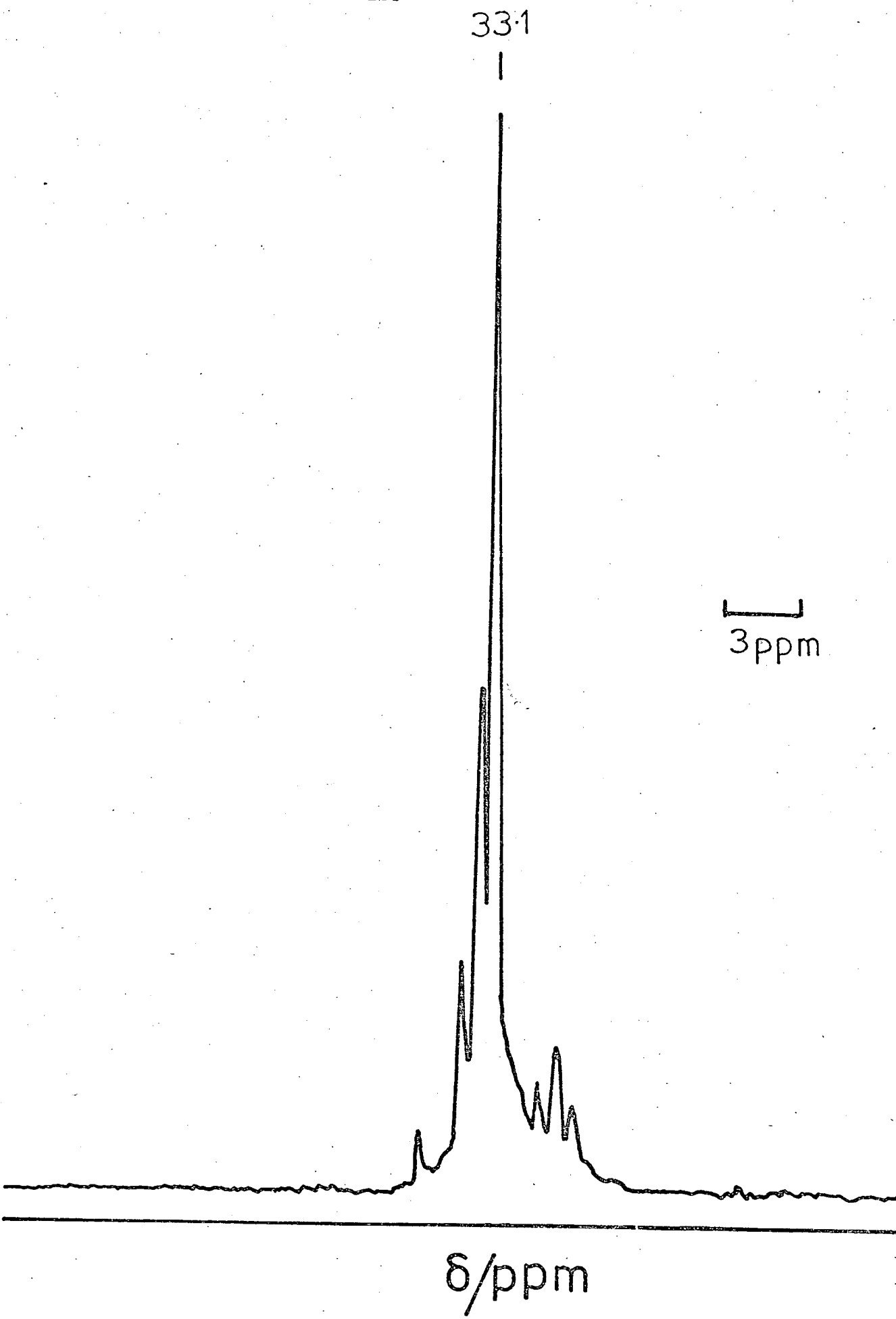
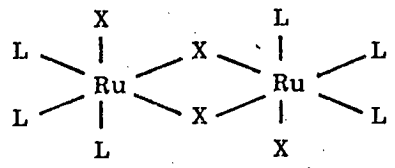
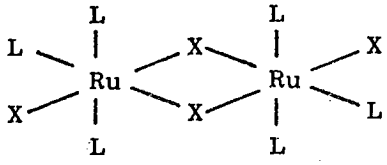


Figure 11 ^{31}P nmr spectrum in $CDCl_3$ at ca 220K of the product of the reaction of $RuCl_2(PEtPh_2)_3$ and $PEtPh_2$ in ethanol.

rearrangement. This mechanism (scheme 2:1) involves the dimerisation of two molecules of $RuCl_2(PEtPh_2)_3$ to form a double halide bridged dimer (XLV)



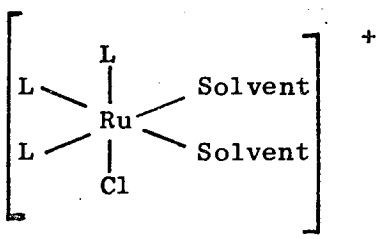
XLVa



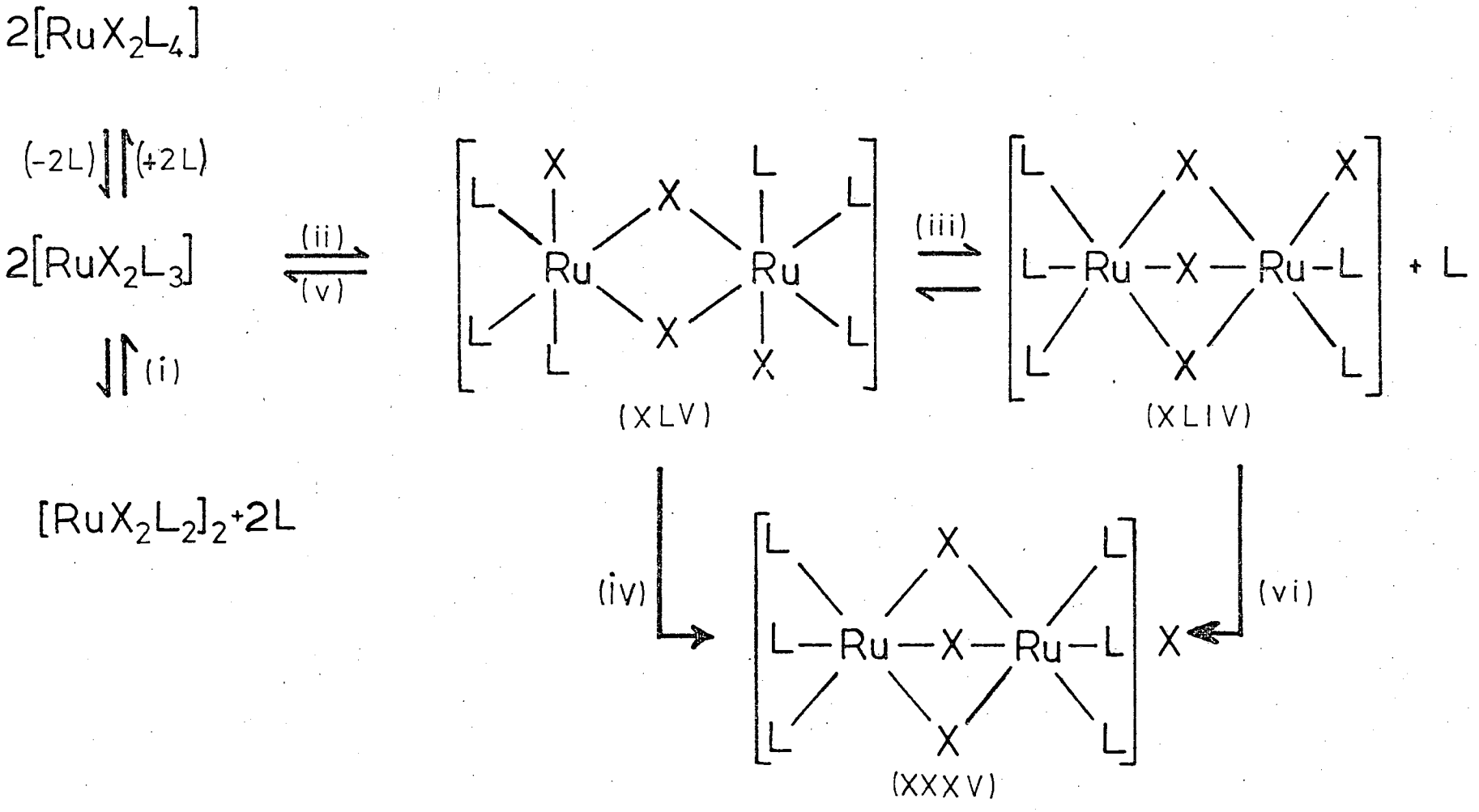
XLVb

The isomer XLVa with all three L groups cis- is preferred to the isomer with two L groups mutually trans- XLVb because the former is much more likely to give an AB_2 resonance pattern in the ^{31}P nmr spectrum and also because it readily leads to structures XLIV and XXXV by simple intramolecular displacement of a phosphine (step iii) or a chloride ligand (step iv) respectively. Precedents for intramolecular rearrangements of this type are provided by the rearrangements proposed for the related complexes $[RuCl_2(\eta\text{-}C_6H_6)]_2$ (169) and $[(\eta\text{-}C_5Me_5)RhCl_2]_2$ (170) which are discussed further in chapters 3 and 4.

However, very recent work has shown that the AB_2 pattern (A,31.0 ppm; B,34.1 ppm; δ_{AB} 126.8Hz ; J_{AB} 63.4Hz) observed in the ^{31}P nmr spectrum of the complex obtained when $RuCl_2(PEtPh_2)_3$ is refluxed with excess $PEtPh_2$ in ethanol is not due to the neutral complex $[RuCl_2(PEtPh_2)_3]_2$ (XLV) but is in fact a cationic species of probable formula $[RuCl(PEtPh_2)_3(EtOH)_2]Cl$ (XLVI)

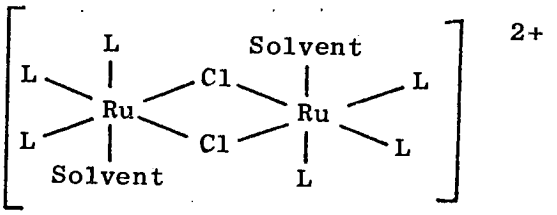


XLVI


2[RuX2L4]
(-2L)
(+2L)
2[RuX2L3]
(ii)
(v)
(i)
(iii)
(XLV)
(XLIV)
+ L
[RuX2L2]2+2L
(iv)
(vi)
(XXXV)

Scheme 2·1

or $[RuCl(PEtPh_2)_3EtOH]_2Cl_2$ (XLVII)[171]



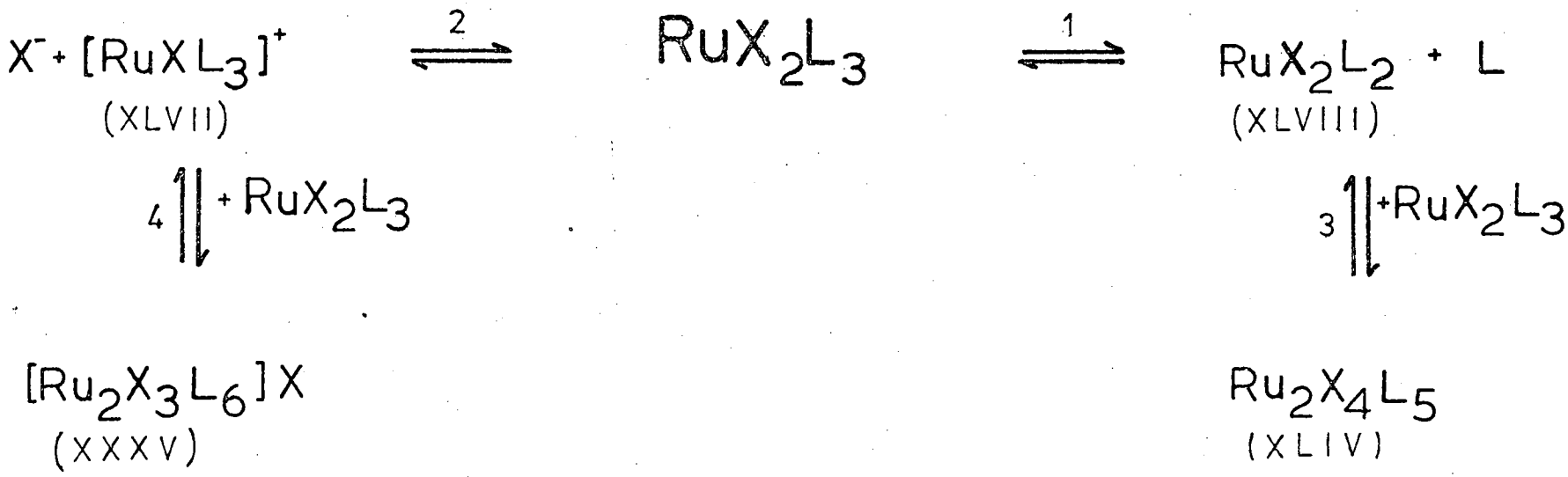
XLVII

The disappearance of this ^{31}P nmr pattern above 220K in $CDCl_3$ with formation of $RuCl_2(PEtPh_2)_3$, $Ru_2Cl_4(PEtPh_2)_5$, $[Ru_2Cl_3(PEtPh_2)_6]Cl$ and $PEtPh_2$ is then readily rationalised by postulating nucleophilic displacement of solvent by chloride ion to form $RuCl_2(PEtPh_2)_3$, which then undergoes facile rearrangement.

A second possibility for the rearrangement mechanism for $RuCl_2(PEtPh_2)_3$ is given in scheme 2.2. RuX_2L_3 (X = Cl, L = $PEtPh_2$) may dissociate either by loss of a phosphine ligand to form the species RuX_2L_2 (XLVIII) (step 1) or by loss of a chloride ligand to form the ionic species $[RuXL_3]^+$ (XLVII) (step 2). These species are then free to react with excess of RuX_2L_3 to form the complexes (XLIV) and (XXXV) respectively. In this scheme both of the dissociative mechanisms (steps 1 and 2) are slow compared with the dimerisation steps (3 and 4). It would be expected that the extent to which each of the dissociation steps 1 and 2 occurred would be governed by the nature of the Ru-X and Ru-L bonds and also by the polarity of the solvent medium.

However, although evidence for the species $[RuXL_3S_2]X$ does exist,[171] there is no evidence in the ^{31}P nmr for the presence of "RuX_2L_2" (other than the tentative assignment of the peak at 47 ppm in the spectrum of $RuCl_2(PEtPh_2)_3$ to this species).

The mechanism for the rearrangement of RuX_2L_3 probably proceeds <u>via direct</u> dimerisation of RuX_2L_3 to form either (XLIV) or (XXXV)


X⁻ + [RuXL3]⁺
(XLVII)
2
RuX2L3
1
RuX2L2 + L
(XLVIII)
4
+ RuX2L3
3
+ RuX2L3
[Ru2X3L6]X
(XXXV)
Ru2X4L5
(XLIV)

Scheme 2·2

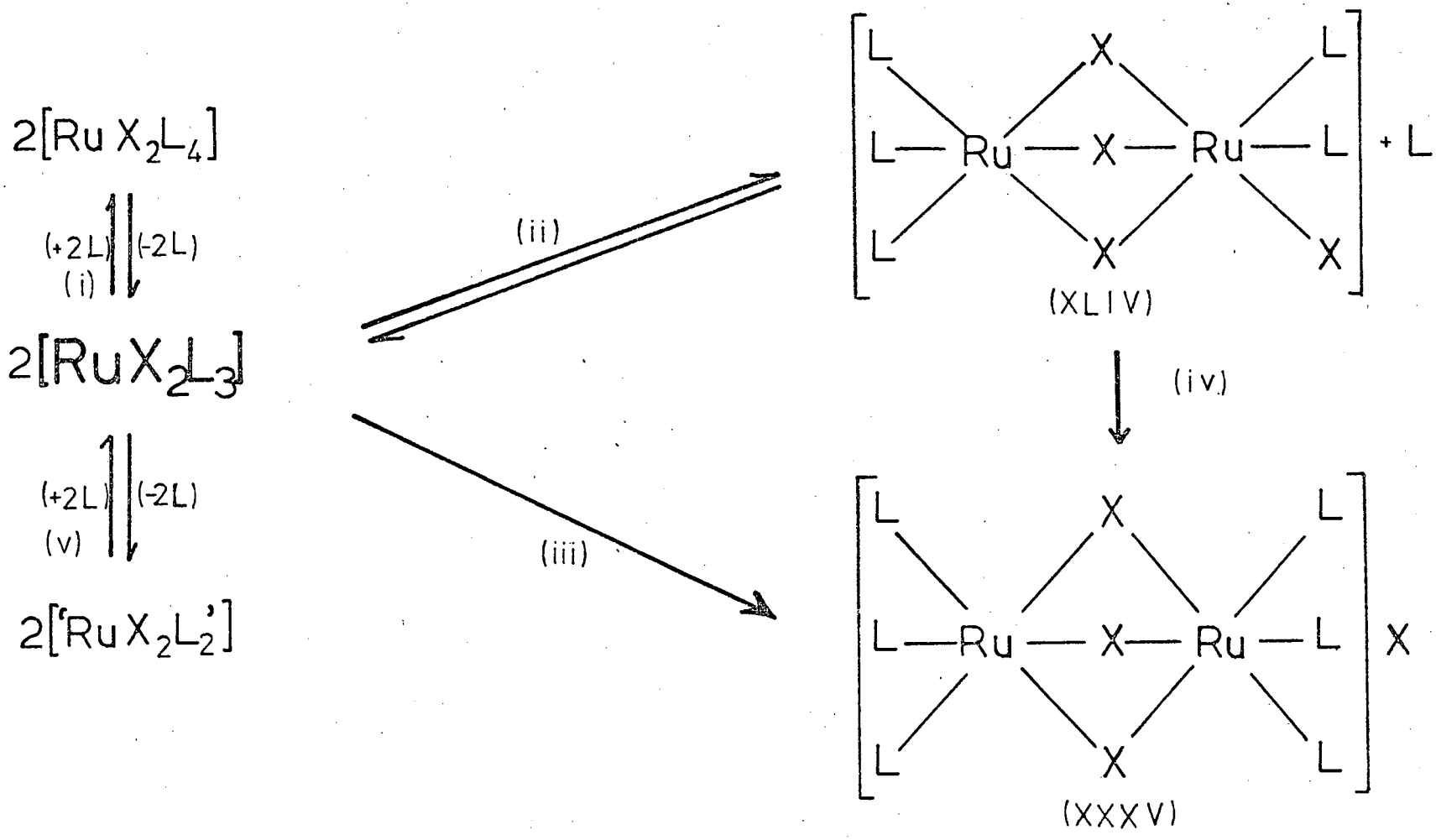
accompanied by concomitant loss of either L or X^- groups respectively (Scheme 2.3). The steps (ii) and (iii) would be sensitive to the nature of the solvent. In non polar solvents e.g. C_6H_6 step(ii) is dominant and no ionic dimer is formed. In more polar solvents step (iii) is favoured: furthermore, slow displacement of the terminal halide group of (XLIV) by $PEtPh_2$ occurs (step (iv)) to give the ionic dimer (XXXV). This step may be reversed by pyrolysing $[Ru_2X_3L_6]X$ in n-propylpropionate in a sealed, evacuated tube at 393K for several hours.(172)

The observation of a broad resonance between 34 and 31 ppm below 315K, in the spectrum of $Ru_2Cl_4(PEtPh_2)_5$, which sharpens to an AB_2 pattern at higher temperatures and then coalesces to a singlet at ambient temperatures appears rather baffling at first sight. However, the high temperature broadening is ascribed to intermolecular exchange of the bound phosphine groups with free $PEtPh_2$ (and this is readily demonstrated by addition of excess $PEtPh_2$). The low temperature broadening (which is also reversible) is attributed to viscosity effects.

C) L = PEt_2Ph

When $RuCl_2(PPh_3)_4$ is refluxed with excess of diethylphenylphosphine in light petroleum (bp 60-80°C) under nitrogen for 24 hours, a dark green solution is formed. Removal of solvent gave a green oil which on treatment with light petroleum (bp 60-80°C) deposited an orange solid. The same orange solid separated out in a more crystalline form, but in smaller yield by carrying out the reaction for 36 hours.

Elemental analyses on this material, although slightly variable, (see experimental section) indicated that the formulation of the complex



Scheme 23

was $RuCl_2L_3$ (L = PEt_2Ph). However, the far infra-red spectrum for this complex was very different from the corresponding complexes where L = $PEtPh_2$; PPh_3, most noticeably in the presence of a strong band at 246 cm^{-1}, indicating bridging chloro-groups. Furthermore, the spectrum was similar to that observed for $Ru_2Cl_4(PEtPh_2)_5$ and molecular weight determinations in benzene indicated that the compound was dimeric. Solutions of the complex in CH_2Cl_2 were non-conducting.

The proton nmr was again uninformative, comprising a multiplet at 7.1δ and a broad resonance at 6.3δ for the phenyl protons, a very broad resonance at 2.2δ for the methylene protons and a multiplet at 0.9δ for the methyl protons.

The ^{31}P nmr spectra in either $CH_2Cl_2/(CD_3)_2CO$ or $CDCL_3$ from 210K to 310K consisted of a sharp singlet at 44.3ppm and an AB_2 pattern of resonances at lower frequency (A,39.1 ppm; B,35.1 ppm; δ_{AB}84.2Hz; J_{AB}29.0Hz) relative intensity 2:3 (fig.12). Below 210K the signals became broad due to viscosity effects, as observed with the corresponding $PEtPh_2$ complex.

Conclusive proof that this complex was a sample of $Ru_2Cl_4(PEt_2Ph)_5$ (XLIV) came from comparing its ^{31}P nmr and far infra-red spectra with a genuine sample prepared by pyrolysing $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ in n-propylpropionate at 393K.[172] The variable analytical data can be explained in terms of the formulation $[Ru_2Cl_4(PEt_2Ph)_5$solv.] in which variable amounts of solvent are trapped in the crystal lattice. Similar analytical difficulties were observed in the original preparation of this complex.[172]

Attempts to isolate a green solid from the reaction between $RuCl_2(PPh_3)_4$ and $PEtPh_2$ were unsuccessful. Also, if $Ru_2Cl_4(PEt_2Ph)_5$ is refluxed in benzene with excess of PEt_2Ph a yellowish-green solution is obtained, but removal of solvent only gave the orange starting material (XLIV).

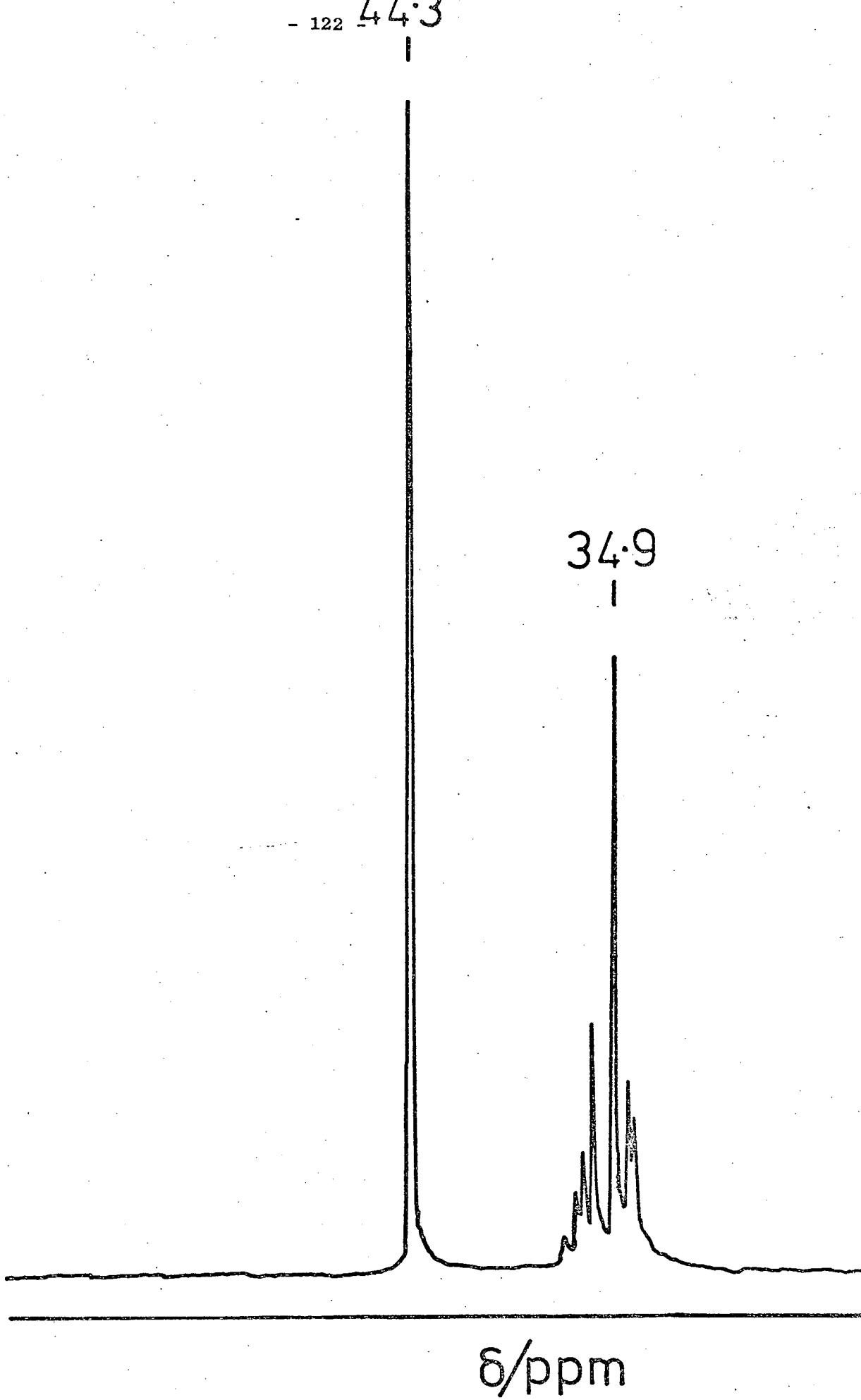


Figure 12 ^{31}P nmr spectrum of $Ru_2Cl_4(PEt_2Ph)_5$ in $CDCl_3$ at ca 295K.

However, a ^{31}P nmr spectrum of this solution at 280K revealed a weak broad resonance at ca 43 ppm (in addition to the $Ru_2Cl_4(PEt_2Ph)_5$ and free $PEtPh_2$ signals) which can be attributed to the presence of some $RuCl_2(PEt_2Ph)_3$ (XXXVII).

If $Ru_2Cl_4(PEt_2Ph)_5$ is refluxed in ethanol with excess PEt_2Ph, the yellow ionic dimer $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ (XXXV) is formed. (^{31}P nmr in $CDCl_3$ is a singlet at 35.4 ppm.)

The product from reaction of $RuBr_2(PPh_3)_4$ with excess PEt_2Ph has only been briefly examined. Again, the analytical data does not unequivocally distinguish between the formulations $RuBr_2(PEt_2Ph)_3$ and $Ru_2Cl_4(PEt_2Ph)_5$ solvent but the ^{31}P nmr spectrum in $CDCl_3$ at 220K which consists of a sharp singlet at 44.2 ppm and a broadened resonance at 35.6 ppm (relative intensity 2:3), indicates the latter.

These reaction products are consistent with the scheme 2.3, $RuCl_2(PEt_2Ph)_3$ being unstable with respect to the triple bridge complex, (XLIV)

d) L = $PClPh_2$

Reaction of $RuCl_2(PPh_3)_4$ with excess $PClPh_2$ in refluxing hexane for three hours gave a non-conducting yellow precipitate. The proton nmr spectrum showed two broad signals in the phenyl region at 7.6δ and 7.2δ.

The ^{31}P nmr spectrum of this compound in $CDCl_3$ is temperature invariant from 210 to 290K and consists of a singlet at 145.7 ppm and an AB_2 pattern at lower frequency (A, 134.5 ppm;B,126.1 ppm; δ_{AB} 341.0Hz; J_{AB} 34Hz) confirming the formulation $Ru_2Cl_4(PClPh_2)_5$.

Attempts to carry out similar reactions in ethanol were unsuccessful due to extensive ethanolysis of the P-Cl bonds with the formation of an intractable mixture of compounds.

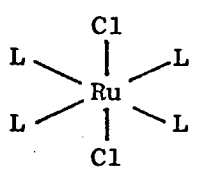
e) L = $PMePh_2$

When $RuCl_2(PPh_3)_4$ is refluxed with excess methyldiphenylphosphine in hexane or light petroleum (bp 60-80°C) for 24 hours, the solution filtered, then evaporated to small volume, orange-yellow crystals are deposited on standing. The complex analysed closely for $RuCl_2(PMePh_2)_4$ and the far infra-red spectrum (see table 2.1) showed the presence of a strong terminal νRu-Cl (316 cm^{-1}).

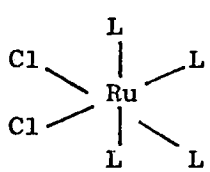
The complex whose solutions are green at ambient but orange at low (<250K) temperatures is initially non-conducting; however the conductivity of the solutions in more polar solvents such as CH_2Cl_2, $CHCl_3$ increases slowly.

The proton nmr spectrum shows a multiplet (7.4, and 7.2δ) for the phenyl protons and a singlet (1.7δ) for the methyl protons, (with smaller peaks at 2.1δ, 1.8δ, 1.6δ) and not the expected doublet or triplet patterns (cf the PMe_2Ph complex-section f). A similar observation has been made for the complex $RuCl_2(PMe_2Bz)_4$.[136]

The ^{31}P nmr spectrum of the complex dissolved in $CDCl_3$ at ca 200K shows a strong singlet at -19.5 ppm and a weak complex pattern of resonances between -5 and -15 ppm. The former is attributed to the complex trans- $RuCl_2(PMePh_2)_4$ (XLVIII) and the weak resonances to the presence of some of the cis- isomer (XLIX), which is distorted due to the steric requirements of the methyldiphenylphosphine ligand to produce an AA'BB' or AA'XX' type of spectrum (fig. 13a)



(XLVIII)



(XLIX)

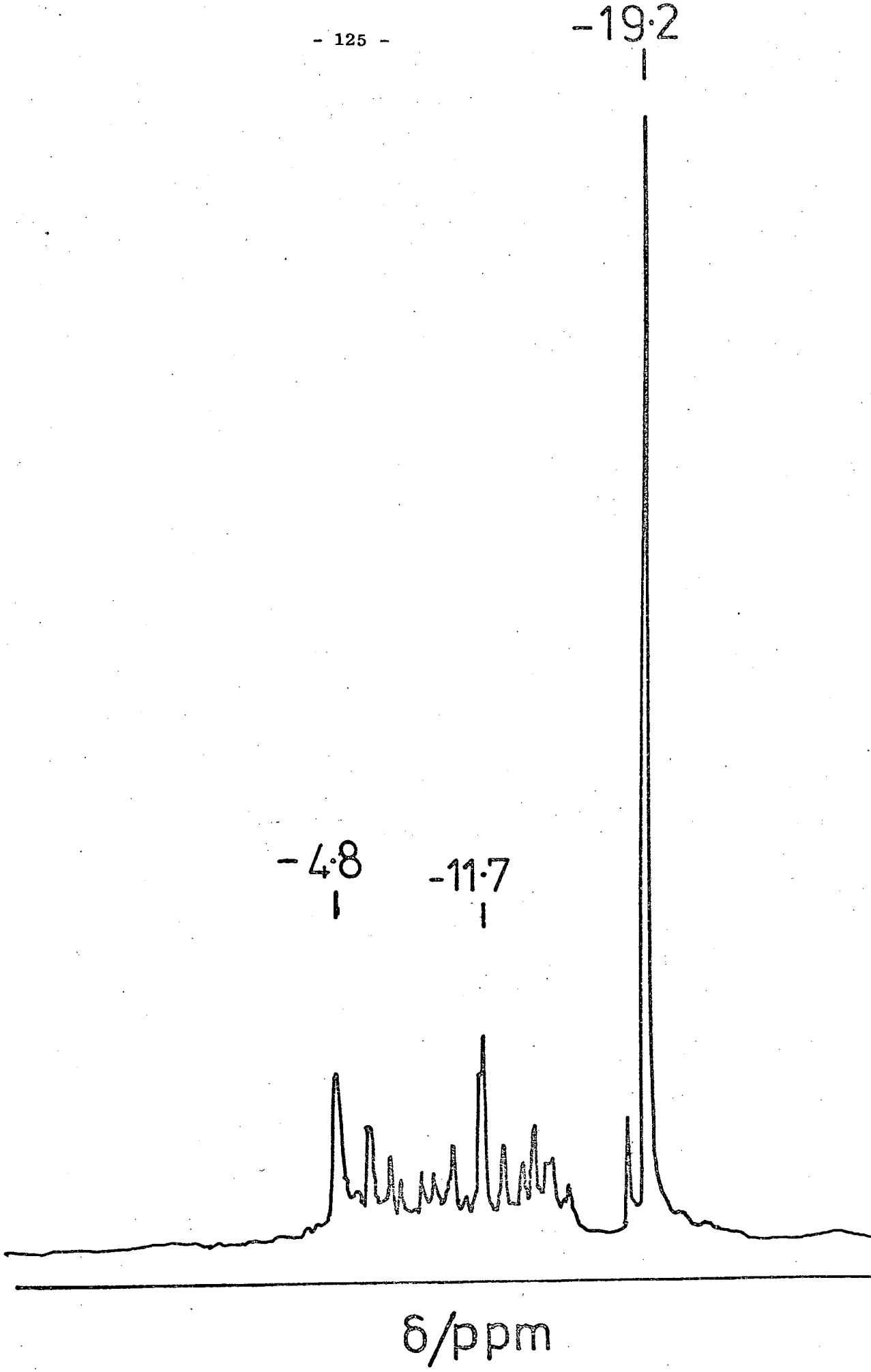


Figure 13a ^{31}P nmr spectrum of $RuCl_2(PMePh_2)_{2-4}$ in $CDCl_3$ at ca 200K.

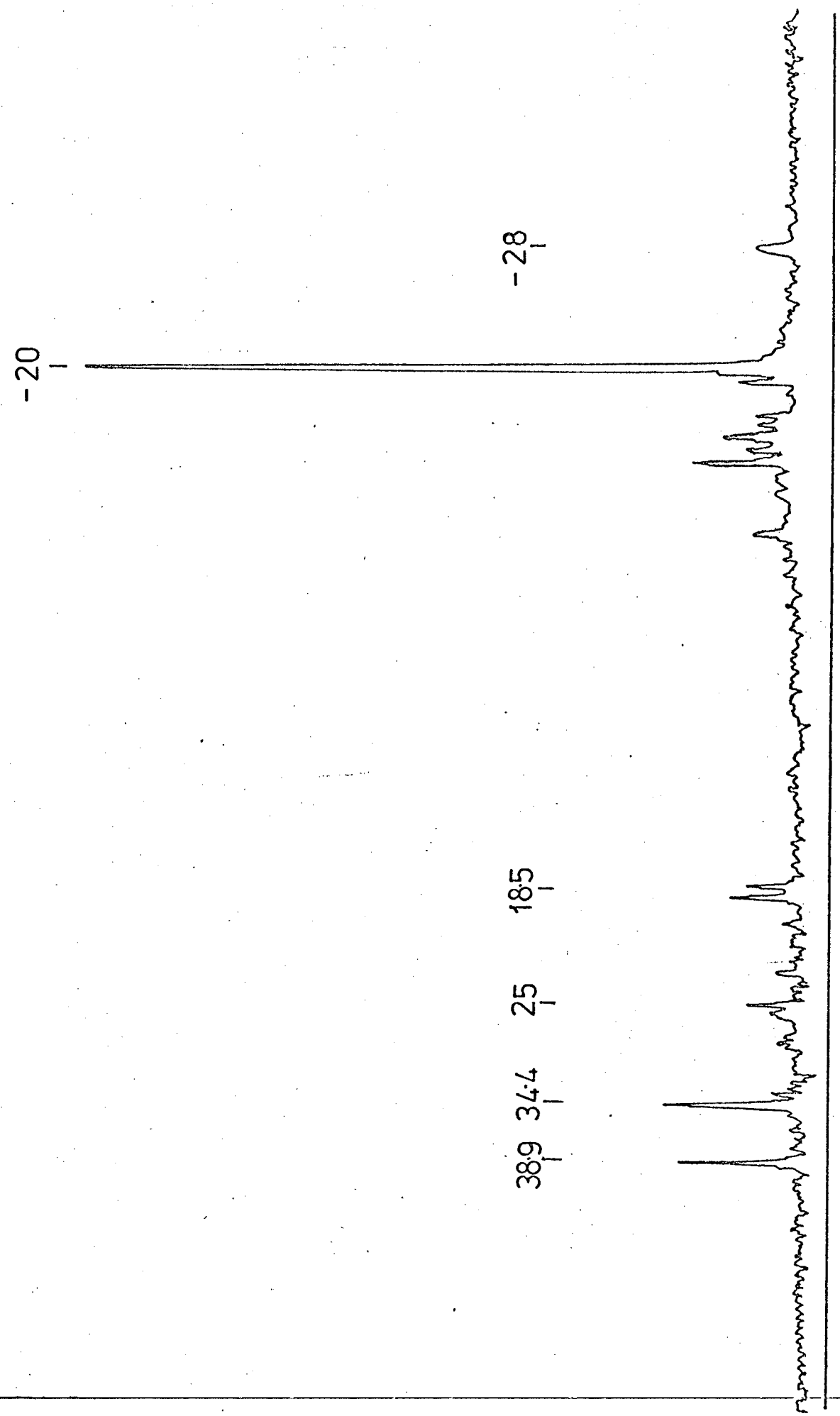


Figure 13b ^{31}P nmr spectrum of $RuCl_2(PMePh_2)_4$ in $CDCl_3$ at ca 250K.

The corresponding hydrido complex $RuH_2(PMePh_2)_4$[130] exists only as the cis- isomer.[131] However solutions of other hydrido complexes RuH_2L_4 (L = $PPh(OMe)_2$, $PPh(OEt)_2$, $(O\text{-}iso\,Pr)_2$ have been shown to consist of a mixture of cis- and trans- isomers.[173]

If, however, the sample of $RuCl_2(PMePh_2)_4$ is first dissolved in $CH_2Cl_2/(CD_3)_2CO$ at room temperature and then cooled to ca 150K, then in addition to the resonances due to $RuCl_2(PMePh_2)_4$ weak signals are observed in the region 20 to 40ppm. The spectrum remains unchanged from 150K to 250K.

At 250K broadening of the resonances between -5 and -15 ppm occurs, whilst the higher frequency resonances increase in intensity, showing singlets at 38.9, 34.4, 25, 19 and 18 ppm; a weak broad resonance is also observed at -28 ppm (free $PMePh_2$) (see fig. 13b).

At 273K the spectrum has altered radically; the resonances due to cis- $RuCl_2(PMePh_2)_4$ have broadened and the singlet at -20 ppm is also broad and has diminished, whereas the peak at -28 ppm (free $PMePh_2$) has increased but remains broad, indicating facile intermolecular exchange is occurring. At the high frequency end of the spectrum, there are strong resonances at 39, 34, 27, 20 and 19 ppm. The entire spectrum shows broadening, indicating that exchange processes are occurring (fig. 14).

At 293K, the low frequency lines, with the exception of free $PMePh_2$ which is very broad, have disappeared. Broadening of the higher frequency lines at 19.3 and 20 ppm occurs and at ca 26 ppm there is a broad resonance on which is superimposed a singlet. The singlet at 34.5 ppm is little different from the spectrum at 273K, but the resonance at 39.2 ppm has sharpened and increased in intensity.

Further broadening of the resonances at 19, 20 and 26 ppm occurs at higher temperatures, but the two high frequency singlets at 39.7

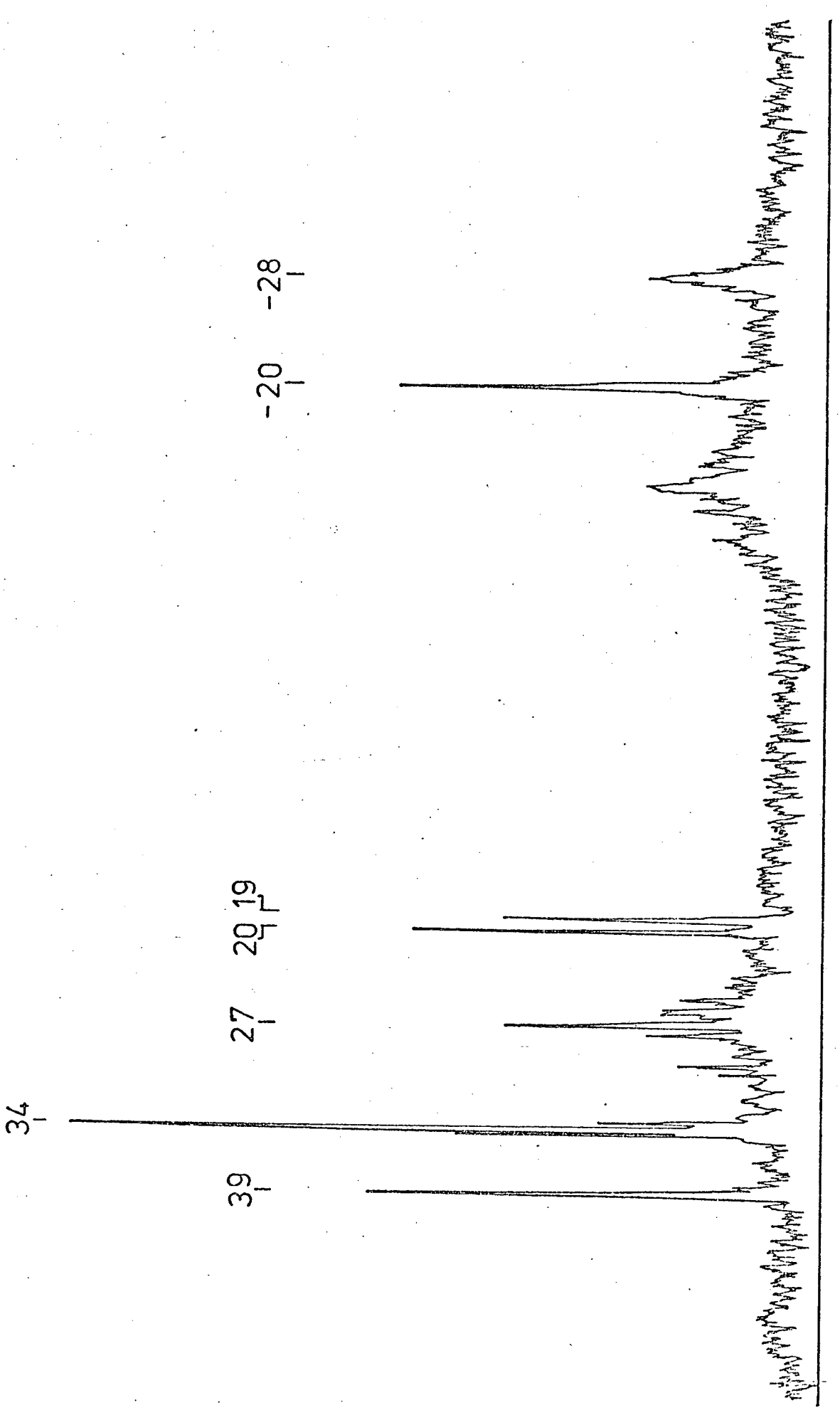


Figure 14 ^{31}P nmr spectrum of $RuCl_2(PMePh_2)_4$ in $CDCl_3$ at ca 273K.

and 34.6 ppm remain sharp. A new sharp resonance also appears at 17.9 ppm which increases with time. This latter signal corresponds to the formation of the triple bridged ionic dimer $[Ru_2Cl_3(PMePh_2)_6]Cl$ (XXXV) (The ^{31}P nmr of a sample of this complex, prepared by reaction of "$RuCl_3 \cdot 3H_2O$" with $PMePh_2$ in 2-methoxyethanol,[129] shows a singlet at 18.4 ppm in $CDCl_3$ at 308K).

On recooling to 210K the ^{31}P nmr spectrum of the complex is similar to that observed previously with the addition of free $PMePh_2$ at -28 ppm and an increase in the intensity of the signals between 20 and 40 ppm.

The behaviour of $RuCl_2(PMePh_2)_4$ may be interpreted in terms of the scheme 2.3. Thus while the monomer in both the cis- and trans- forms is stable at temperatures up to 230K, above this temperature it dissociates to form either fluxional $RuCl_2L_3$ or "$RuCl_2L_2$" (singlet at 39 ppm) and associates to form $Ru_2Cl_4(PMePh_2)_5$ (XLIV). The presence of the latter may be confirmed by comparison of the ^{31}P nmr spectrum of a genuine sample of $Ru_2Cl_4(PMePh_2)_5$ prepared by the pyrolysis of $[Ru_2Cl_3(PMePh_2)_6]Cl$ at ca 400K. Between ca 240K and 280K the ^{31}P nmr spectrum in $CDCl_3$ (fig. 15) comprises an AB_2 pattern (almost AX_2) (A,28.3ppm; B,19.9ppm; δ_{AB} 324.0Hz; J_{AB} 26Hz) and a singlet (35.1 ppm). Below 240K the spectrum is affected by viscosity broadening and above 280K reversible decomposition occurs.

The AB_2 pattern is not well resolved in the spectra of $RuCl_2(PMePh_2)_4$ because of exchange between bound phosphine groups and free $PMePh_2$, as may be demonstrated by adding excess of methyldiphenylphosphine to a solution of $Ru_2Cl_4(PMePh_2)_5$.

Solutions of $Ru_2Cl_4(PMePh_2)_5$ are green (cf. $RuCl_2(PMePh_2)_4$ which are also green at ambient temperatures): however an addition of excess

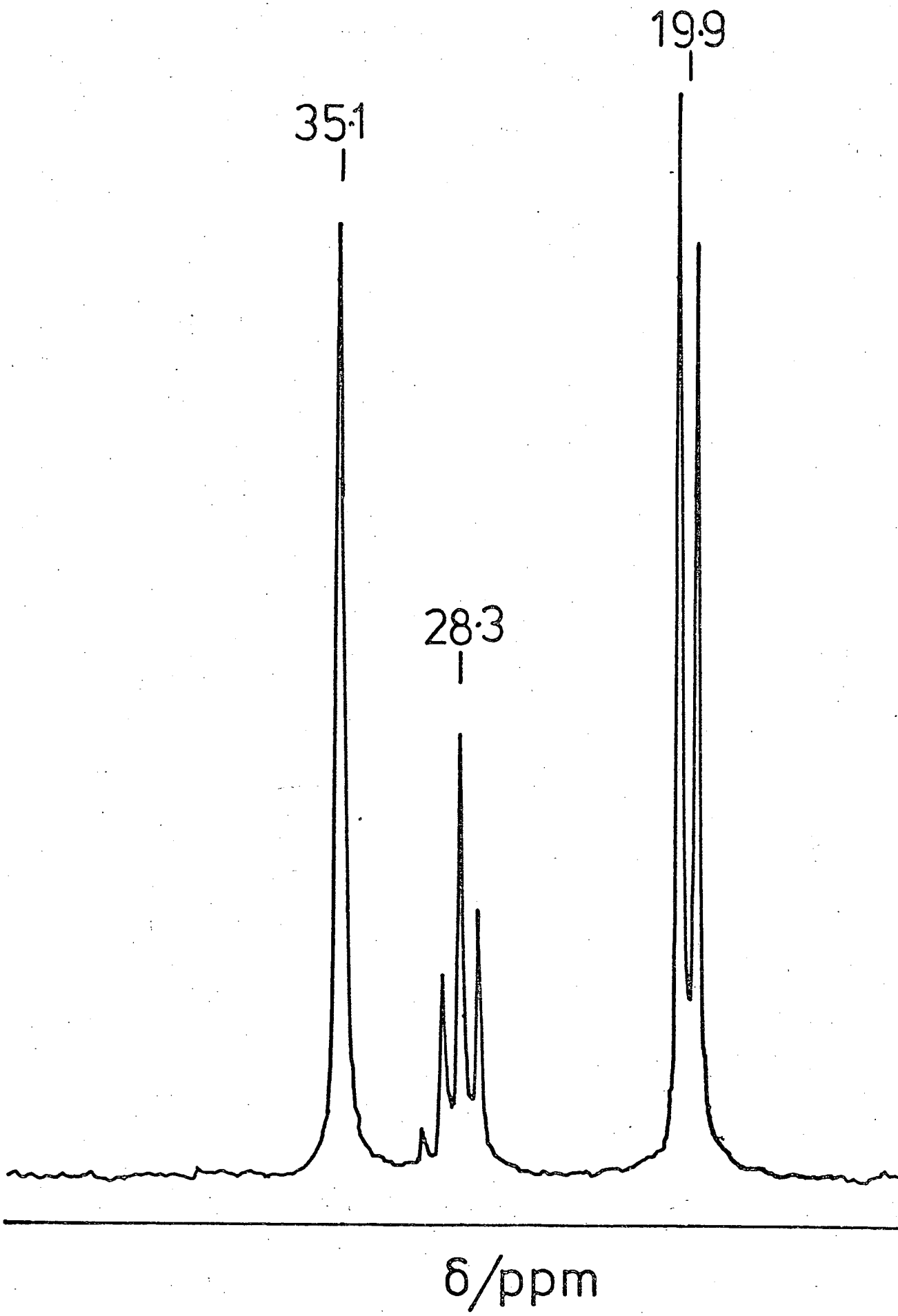


Figure 15 ^{31}P nmr spectrum of $Ru_2Cl_4(PMePh_2)_5$ in $CDCl_3$ at ca 250K.

(1:5 molar ratios) of free tertiary phosphine, the solution becomes orange. The ^{31}P nmr spectrum of this solution in $CDCl_3$ at ca 260K shows a very broad resonance at -24 ppm (free $PMePh_2$ - the resonance is broad and shifted 4 ppm to high frequency indicating exchange), a strong singlet at -19 ppm (trans- $RuCl_2(PMePh_2)_4$) and a complex pattern between -5 and -19 ppm (cis- $RuCl_2(PMePh_2)_4$). In addition there is a broad resonance at 22.4 ppm and a sharp resonance at 31.3 ppm ($Ru_2Cl_4(PMePh_2)_5$ - shifts ca 4 ppm to low frequency, indicating rapid exchange of bound phosphine groups with free $PMePh_2$). These observations illustrate the reversibility even in more polar solvents ($CDCl_3$) of the steps (i) and (ii) (scheme 2.3) although here, no definite evidence is observed for the intermediate $RuCl_2(PMePh_2)_3$.

The corresponding hydrido complex $RuH_2(PMePh_2)_4$ is much more thermally stable than the chloro-complex decomposing (reversibly) only at 400K.[131] The added stability of these complexes is presumably due to the instability of such complexes as (XLIV) and (XXXV) when X = H.

f) L = PMe_2Ph

Reaction of $RuCl_2(PPh_3)_4$ with excess dimethylphenylphosphine in refluxing light petroleum (bp 60-80°C) for 3 hours gave a crystalline yellow precipitate which analysed closely for $RuCl_2(PMe_2Ph)_4$. This compound can also be prepared by reaction of mer- $RuCl_3(PMe_2Ph)_3$ with excess PMe_2Ph in hexane.[174] Although this compound is quite stable in the solid state, it rapidly rearranges in solvents such as CH_2Cl_2 to give $[Ru_2Cl_3(PMe_2Ph)_6]Cl$. This process can be monitored by the steady increase in the conductivity of a CH_2Cl_2 solution with time (see fig. 16). After ca 5 hours at 300K, removal of CH_2Cl_2 gives a quantitative yield of $[Ru_2Cl_3(PMe_2Ph)_6]Cl$.

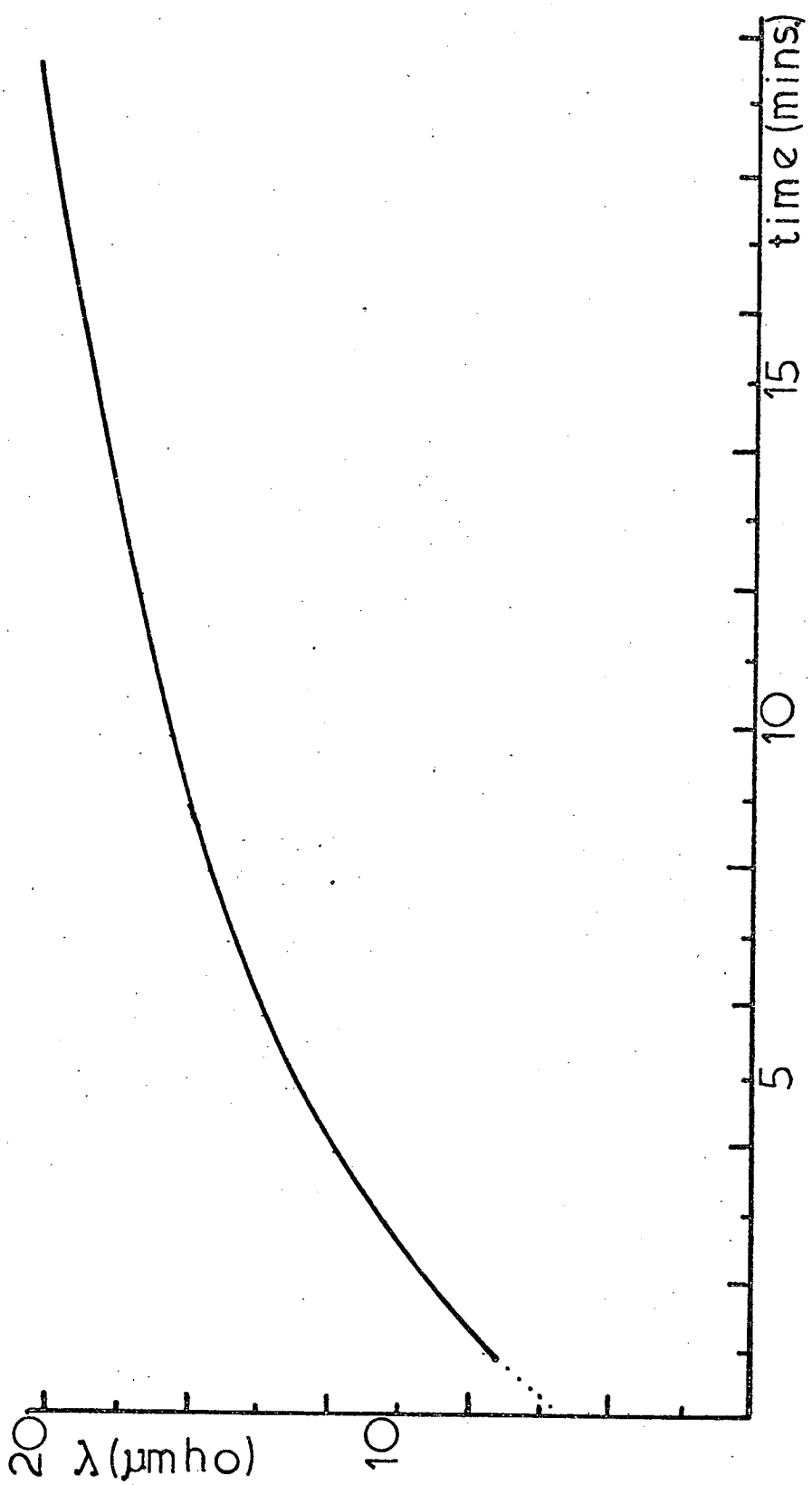


Figure 16 Graph of conductivity V. time for a 10^{-3}M solution of $RuCl_2(PMe_2Ph)_4$ in CH_2Cl_2.

However, the complex is quite stable if it is dissolved in less polar solvents such as $CDCl_3$ and kept at temperatures below 270K. Thus, the ^{31}P nmr spectrum in $CDCl_3$ solution, from 210 - 270K shows two 1:2:1 triplets at 15.8 ppm and -6.5 ppm (J_{pp} 30.0Hz) (fig. 17a) consistent with the cis- configuration (XLIX) (cf. $RuH_2(PMe_2Ph)_4$).[173]

Above this temperature rapid conversion to the ionic dimer occurs as observed by the appearance of a sharp singlet at 22.0 ppm and a decrease in the intensity of the two triplets (fig. 17b). Rather surprisingly, there is no evidence for any intermediates such as $RuCl_2(PMe_2Ph)_3$, nor for the formation of any $Ru_2Cl_4(PMe_2Ph)_5$ or even free PMe_2Ph. However, the absence of the latter is due to fast intermolecular exchange at temperatures above 270K between PMe_2Ph and the ionic dimer (XXXV) as is readily demonstrated by adding free dimethylphenylphosphine to $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ in $CDCl_3$ solution.

The failure to observe any of the other intermediates proposed in the scheme 2.3 does not necessarily invalidate the occurrence of this general rearrangement mechanism in this instance. The known high affinity of PMe_2Ph for ruthenium(II)[175] is probably responsible for the short-lived nature of species such as $RuCl_2L_3$ and $Ru_2Cl_4L_5$ (L = PMe_2Ph). This affinity is further demonstrated by the failure of the pyrolysis reaction, even at temperatures above 400K to convert $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ to $Ru_2Cl_4(PMe_2Ph)_5$ (cf $PEtPh_2$, PEt_2Ph, $PMePh_2$) and also the preference for chloride loss to form (XXXV) over phosphine loss to form (XLIV).

The ^1H nmr spectrum of the complex in $CDCl_3$ at 250K shows two triplets at 1.60δ and 1.48δ corresponding to the methyl protons of the mutually trans- and cis- phosphines respectively. This pattern is very similar to that observed for cis- $RuH_2(PMe_2Ph)_4$,[173] the trans phosphines in both complexes producing a virtually coupled 1:2:1 triplet, indicating that Jpp trans is very large. However, whilst the cis- phosphines of

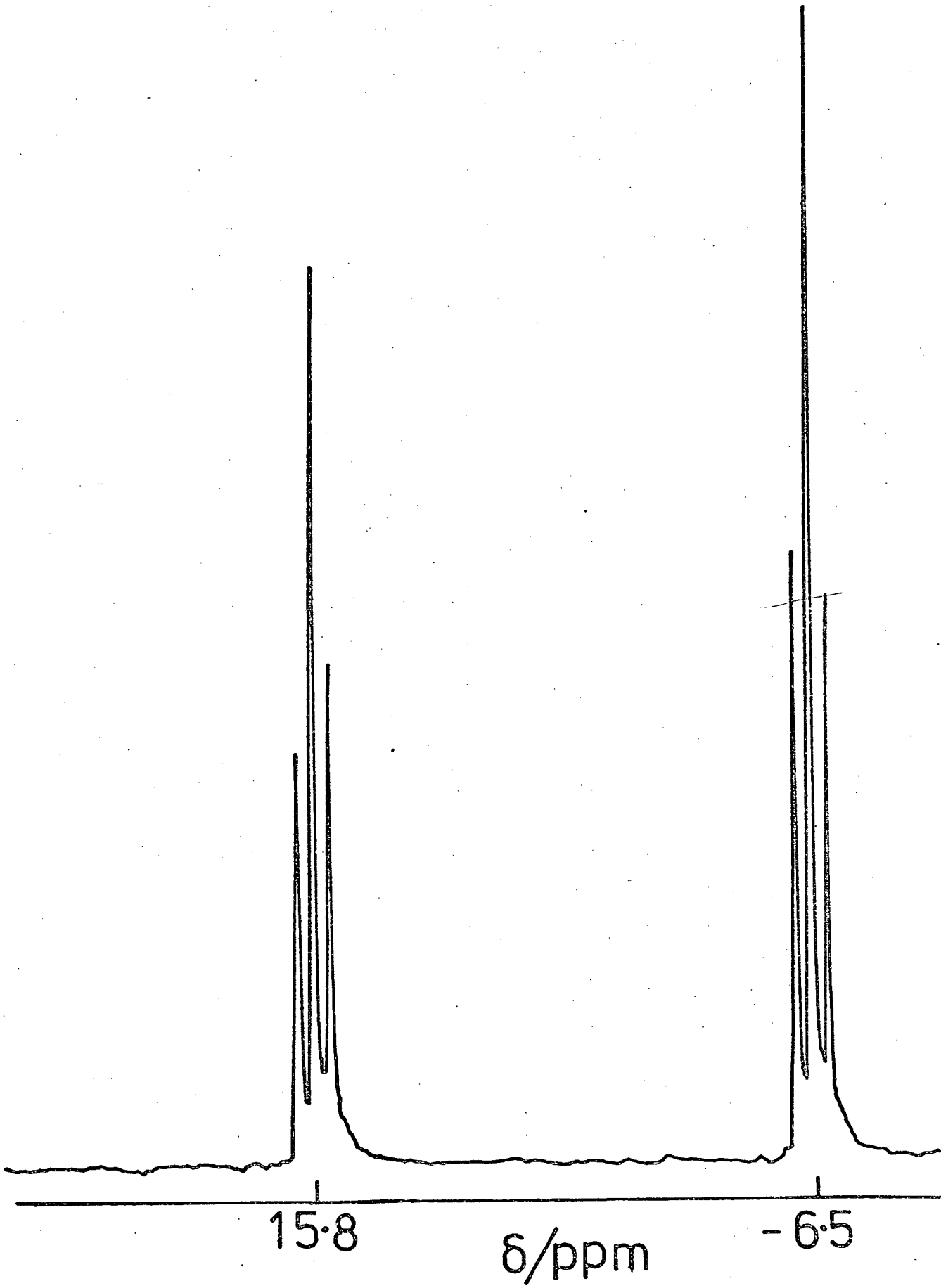


Figure 17a ^{31}P nmr spectrum of $RuCl_2(PMe_2Ph)_4$ in $CDCl_3$ at ca 250K.

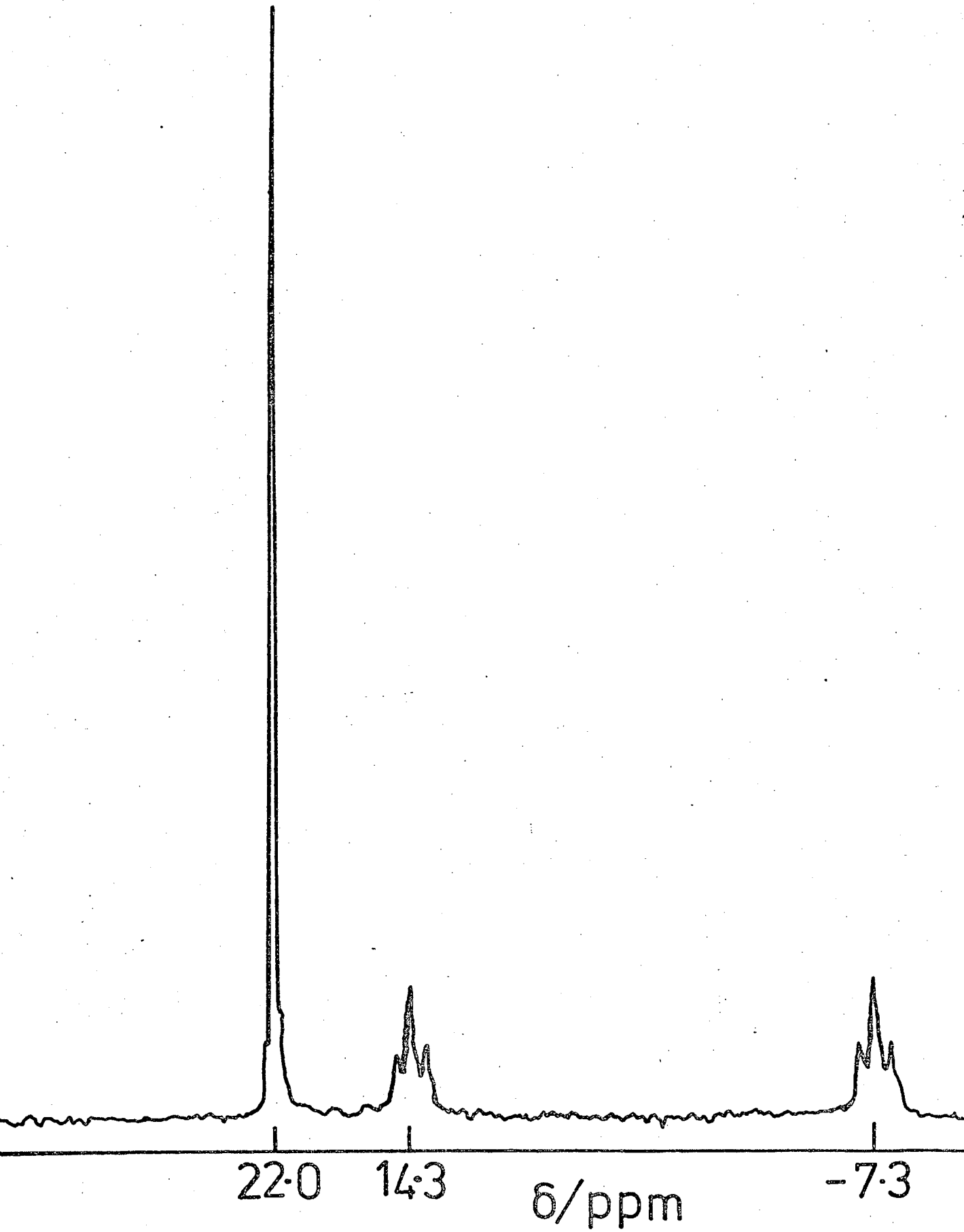


Figure 17b ^{31}P nmr spectrum of $RuCl_2(PMe_2Ph)_4$ in $CDCl_3$ at ca 305K.

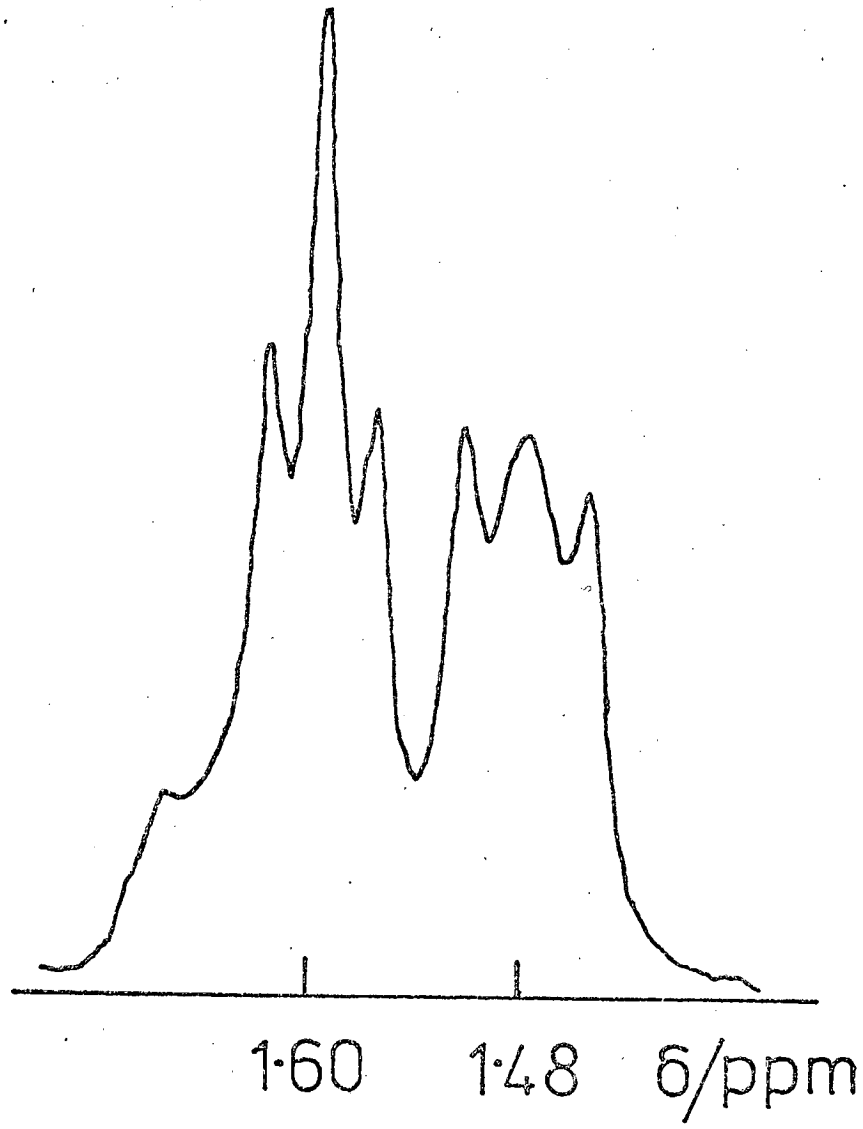


Figure 18a The methyl region of the ^{1}H nmr spectrum of $RuCl_2(PMe_2Ph)_4$ in $CDCl_3$ at ca 250K.

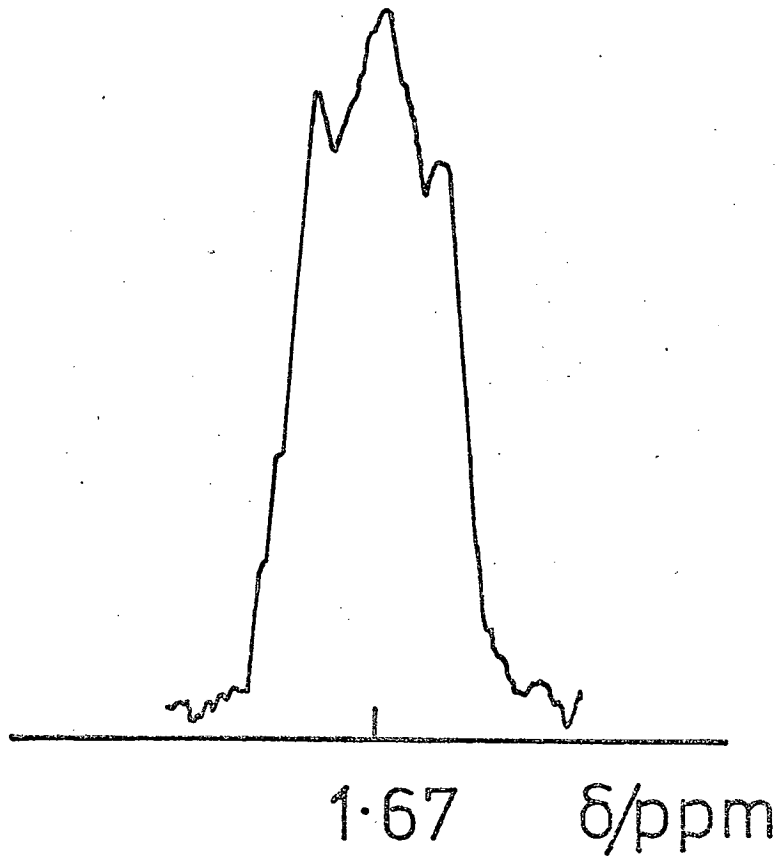


Figure 18b The methyl region of the ^{1}H nmr spectrum of $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ in $CDCl_3$ at ca 308K.

$RuH_2(PMe_2Ph)_4$ give rise to a sharp doublet (i.e. J_{pp} (cis-) is effectively zero), in the chloro-complex the cis- phosphorus nuclei are much more strongly coupled giving rise to a "pseudo-triplet", i.e. a sharp doublet with a broad hump situated between the doublet (see figs. 18a, 18b). This signifies a relatively large J_{pp} compared to $|J_{PH} + J_{PH^1}|$ [176] (cf cis-$Ru(S_2PMe_2)_2(PMe_2Ph)_2$) [177]

At higher temperatures, the ^1H nmr spectrum converts to a single "pseudo-triplet" at 1.67δ characteristic of $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ (fig. 18b).

At 250K, the ^{31}C proton noise decoupled nmr spectrum of $RuCl_2(PMe_2Ph)_4$ in $CDCl_3$ shows a pattern similar to the ^1H nmr spectrum, namely two triplets for the methyl carbons at 15.8 and 21.4 ppm (J_{PC} 15Hz), two triplets for the quaternary carbon atoms of the phenyl rings (140 ppm, J_{PC} 17Hz) and a complex series of doublets for the remaining phenyl carbons between 126 and 139 ppm.

2.3 Conclusions

These studies clearly show that earlier attempts to generate monomeric ruthenium(II) halide, tertiaryphosphine complexes by direct reaction of "$RuCl_3.3H_2O$" and PR_3 have generally been unsuccessful because of the facile rearrangement processes to form dimeric compounds. The driving force for these rearrangements is presumably the high stability of six coordinate ruthenium(II) ($4d^6$) complexes containing a triple halide bridge. However, the relative stabilities of the various products are very sensitive to both the solvent employed and the steric and electronic properties of the tertiary phosphine. Thus, only when bulky tertiary phosphines such as PPh_3 or $P(p\text{-}MeC_6H_4)_3$ are used are monomeric compounds isolated from the trichloride since steric constraints inhibit associative rearrangement reactions.

However, in this instance, dissociative processes become of increasing importance and the compounds exhibit catalytic activity. For the

smaller $PEtPh_2$, although $RuCl_2(PEtPh_2)_3$ can be isolated *via* $RuCl_2(PPh_3)_4$, it readily rearranges to $Ru_2Cl_4(PEtPh_2)_5$ in non-polar, and $[Ru_2Cl_3(PEtPh_2)_6]Cl$ in polar media. For the even smaller PEt_2Ph and $PClPh_2$, the monomeric *tris*- complexes cannot be isolated but rapidly dimerise in the absence of a large excess of phosphine to give $Ru_2Cl_4L_5$.

Although $PMePh_2$ and PMe_2Ph are able to form the *tetrakis*-complexes, rapid rearrangement to $Ru_2Cl_4(PMePh_2)_5$ and to $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ respectively are observed in solution.

Studies with other group 5B donor ligands such as tertiary phosphinites, phosphonites and phosphites, now in progress[171] confirm the applicability of this scheme (2.3) to a wider range of ligands.

TABLE 2:1

Far Infra-red Spectra (400 - 150 cm^{-1}) of some Ruthenium Tertiary Phosphine Complexes (shoulders underlined).

Compound	ν(RuX) cm^{-1}	Other Bands (cm^{-1})
$RuCl_2(PPh_3)_3$	315s	298w,284w,275w,266w,257w,235m, 230,197m,183m,175w,155w.
$RuBr_2(PPh_3)_3$	249w	307s,277w,266m,257m, 232s,196m,184w.
$[RuCl_2(PPh_3)_2acetone]_2$	323vs,250m	329,290m,280w,267m,260w,239w, 224s,216m,196w,192w,182s,154w.
$RuCl_2(PEtPh_2)_3$	327s	296w,272m(br),246w,173m(br).
$RuBr_2(PEtPh_2)_3$	252w	322w,317w,290w,265m(br),190w.
$[Ru_2Cl_3(PEtPh_2)_6]Cl$	250m	296w,269s,208w,180m.
$Ru_2Cl_4(PEtPh_2)_5$	321m,260m(br)	300w,206w.
$[Ru_2Cl_3(PEt_2Ph)_6]Cl$	250s	319w,299m,217w.
$Ru_2Cl_4(PEt_2Ph)_5$	311s,246s	291m,264w,217w,155w.
$Ru_2Br_4(PEt_2Ph)_5$	246s	360w,334w,326w,305,290m,250, 215w(br).
$RuCl_2(PMePh_2)_4$	316s	348s,271w(br),253w,245w,232m, 210w,183m,166w,154w.
$RuBr_2(PMePh_2)_4$	245m	348s,302w,269w,251,231m,181m, 155w.
$[Ru_2Cl_3(PMePh_2)_6]Cl$	245m	363w,300w(br),283m(br),268w, 226w,218w,198vw,184w.
$Ru_2Cl_4(PMePh_2)_5$	311s,238m	342m,320,300w,286,279s,269,251w,183w
$RuCl_2(PMe_2Ph)_4$	292s	358s,341s,282s,248,234vs,189w.
$RuBr_2(PMe_2Ph)_4$	230s	352m,338s,283m,182m,167m.
$[Ru_2Cl_3(PMe_2Ph)_6]Cl$	241s	288w,263w,177m.

2.4 Experimental

Microanalyses were by A. Bernhardt, West Germany and the University of Edinburgh, Chemistry Department. Molecular weights were determined on a Perkin-Elmer-Hitachi 115 osmometer in benzene at 37°. I.r. spectra were recorded in the region 4000-250 cm^{-1} on Perkin Elmer 457 and 225 grating spectrometers using Nujol and Hexachlorobutadiene mulls on caesium iodide plates and in the region 400-150 cm^{-1} on a Beckman RIIC IR 720 far infrared spectrometer using pressed polythene discs. ^{1}H nmr spectra were obtained on a Varian Associates HA-100 Spectrometer equipped with variable temperature attachment and ^{13}C and ^{31}P nmr spectra on a Varian Associates XL100 spectrometer operating in the Pulse and Fourier Transform mode at 25.2MHz and 40.5MHz respectively. Chemical shifts are reported in ppm to high frequency of tetramethylsilane and 85% H_3PO_4 respectively. Conductivity measurements were made on a model 310 Portland Electronics conductivity bridge. Mp's were determined with a Kofler hot-stage microscope and are uncorrected. $RuX_2(PPh_3)_{3 \text{ or } 4}$ (X = Cl,Br) were prepared as described earlier[114] and their ^{31}P nmr spectra (X = Cl) were obtained on solutions which had been thoroughly deoxygenated by "freeze-thaw" techniques and then sealed into 5mm nmr tubes. For the other tertiary phosphine complexes which are much less air sensitive, purging the solvents by refluxing in a steam of nitrogen was sufficient to eliminate formation of phosphine oxides and other oxidation products for the duration of the spectroscopic studies. Pure samples of the ionic dimers $[Ru_2Cl_3L_6]Cl$ (L = $PEtPh_2$, PEt_2Ph, $PMePh_2$, PMe_2Ph) and of the neutral dimers $Ru_2Cl_4L_5$, (L = $PEtPh_2$, PEt_2Ph, $PMePh_2$) were obtained by literature methods.[128,129;172]

Reaction of $RuCl_2(PPh_3)_3$ with nitromethane and sodium tetraphenylborate.

$RuCl_2(PPh_3)_3$ (0.3g) was mixed with $NaBPh_4$ (0.1g) and nitromethane (50 cm^3) was added. The mixture was shaken under nitrogen for 1 hour. The resulting solution was filtered to remove excess $NaBPh_4$ and an equal quantity of ethanol was added to the yellow filtrate which was then evaporated under vacuo. The resulting yellow-green oil was extracted into hot ethanol. The ethanol was then removed slowly under vacuo until a pale yellow precipitate separated. The solid was filtered and washed with water, ethanol and diethylether.

Found: C, 72.1; 71.4; 68.7; 70.0%
H, 5.9; 5.7; 5.2; 5.6%
N, 3.6; 2.5; 3.4; 2.5%.

For discussion of ^{31}P nmr see p 98.

Reaction of $RuCl_2(PPh_3)_3$ with methylcyanide and sodium tetraphenylborate.

$RuCl_2(PPh_3)_3$ (0.3g) was added to CH_3CN (30 cm^3) and an excess (0.3g) of $NaBPh_4$ was added. The solution was shaken under nitrogen for 2 days. It was then filtered and the filtrate evaporated under vacuo to ca 2 cm^3. An excess of ethanol was added and the resulting off-white precipitate filtered and washed with methanol, ethanol and diethylether.

Found: C, 73.3; H, 5.5; N, 3.4%

The filtrate and washings were evaporated under vacuo to small volume when a bright yellow solid separated. This was filtered off and washed with ethanol and diethylether.

Found: C, 68.3; H, 5.0; N, 2.5%

Dichlorotris(ethyldiphenylphosphine)ruthenium(II):-

$RuCl_2(PPh_3)_4$ (1.0g) was refluxed in degassed hexane (30 cm^3) with ethyldiphenylphosphine (0.40 cm^3) under nitrogen for 18 h. The resulting green crystalline precipitate was filtered off, washed thoroughly with light petroleum (bp 40 - 60°C) to remove any free phosphine and dried in vacuo at 40°C (Yield: 0.59g; 88%)m.p. 142°C (decomp) [Found: C, 62.0; H, 5.7; Cl, 9.0. Calc. for $C_{42}H_{45}Cl_2P_3Ru$:- C, 61.9; H, 5.5; Cl, 8.7%]. I.r. (mull -2000-400 cm^{-1}) 1583w, 1570m, 1485s, 1460m, 1430s, 1380m, 1306w, 1270w, 1240w, 1190m, 1158m, 1118w, 1095s, 1030s, 996m, 970w, 755-730s(br), 700-690s(br), 660m, 555s, 630-620s(br), 495m, 480w, 460m, 448m, 435m.

Dibromotris(ethyldiphenylphosphine)ruthenium(II):-

As for the chloro complex but using $RuBr_2(PPh_3)_4$ (0.40g) and ethyldiphenylphosphine (0.40 cm^3) (0.22g; 80%) m.p. 156-158°C [Found: C, 55.4; H, 5.1. Calc. for $C_{42}H_{45}Br_2P_3Ru$: C, 55.8; H, 5.0%] I.r. (mull -2000-400 cm^{-1}) identical to that of $RuCl_2(PEtPh_2)_3$.

Tri-μ-chloro-[tris(ethyldiphenylphosphine]ruthenium(II)] [Chloro bis-(ethyldiphenylphosphine)ruthenium(II)]:-

$RuCl_2(PEtPh_2)_3$ was dissolved in dichloromethane at room temperature to give a green solution and then solvent removed under vacuo to leave a sticky residue. Addition of light petroleum (bp 60 - 80°C) then gave an orange-brown solution and a green residue. Partial removal of solvent precipitated the orange-brown product m.p. 118 - 122°C (decomp) [Found: C, 59.1, 59.2; H, 5.4, 5.6. M(in C_6H_6)1132. Calc. for $C_{70}H_{75}Cl_4P_5Ru_2$: C, 59.4; H, 5.3% M 1414]. I.r. (mull 2000-400 cm^{-1}) 1580vw, 1485m, 1455w, 1435s, 1380w, 1318w, 1092m and br, 1040m, 990w, 750sh, 745sh, 739s, 699s, 690s, 640w, 538sh, 520s, 490w, 450-430 m and br.

Reaction of $RuCl_2(PEtPh_2)_3$ with $PEtPh_2$ in ethanol:-

$RuCl_2(PEtPh_2)_3$ (0.14g) was refluxed in degassed ethanol (50 cm^3) with ethyldiphenylphosphine (0.10 cm^3) under nitrogen for 3 h. The solution was filtered hot to remove excess green starting material and then solvent removed under vacuo. Addition of light petroleum (bp 60 - 80°C) to the resulting oil gave a yellow solid which analysed closely for "$RuCl_2(PEtPh_2)_3$" [Found: C, 60.6; H, 5.7. Calc. for "$RuCl_2(PEtPh_2)_3$" C, 61.9; H, 5.5%]. ^{31}P nmr studies indicated this material to be a mixture of $[Ru_2Cl_3(PEtPh_2)_6]Cl$ and $[RuCl(PEtPh_2)_3(EtOH)_2]Cl$.

Tri-μ-chloro-[tris(diethylphenylphosphine)ruthenium(II)][Chloro bis-(diethylphenylphosphine) ruthenium(II)]:-

a) $RuCl_2(PPh_3)_4$ (0.40g) in degassed light petroleum (bp 60 - 80°C) (50 cm^3) was refluxed with diethylphenylphosphine (0.35 cm^3) for 24 h under nitrogen. The resulting dark green solution was filtered and evaporated to a green oil from which the orange product separated on addition of light petroleum (bp 60 - 80°C). The product was filtered and washed with light petroleum (bp 40 - 60°C) to remove any free PPh_3 (0.11g, 58%) m.p. 125 - 127°C [Found: C, 53.5, 52.4, 51.9; H, 6.7, 6.8, 6.8; Cl, 10.5; M (in C_6H_6) 1115. Calc. for $C_{50}H_{75}Cl_4P_5Ru_2$: C, 51.1; H, 6.4; Cl, 12.1% M 1174]. The variable analytical figures are ascribed to differing amounts of solvent of crystallisation (cf the preparation of $Ru_2Cl_4(PEt_2Ph)_5$ from $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ and n-propylpropionate).[172] I.r. (mull 2000-400 cm^{-1}) 1585w, 1570vw, 1481w, 1465w and br, 1434s, 1416w, 1380m, 1320w, 1263w, 1242m and br, 1189w, 1157w, 1100m-s, 1073w, 1038 and 1032s, 999w, 984w, 810w and br, 762sh, 748sh, 732s, 721sh, 705s, 687w, 630m and br, 540m, 527s, 505s, 500sh, 470m, 450m, 410w.

b) The same compound is made directly by refluxing $RuCl_2(PPh_3)_4$ (0.40g) in light petroleum (bp 60 - 80°C) with diethylphenylphosphine (0.35 cm^3) for 36 h when the orange crystals are precipitated.

Tri-μ-bromo-[tris(diethylphenylphosphine)ruthenium(II)][bromo bis-(diethylphenylphosphine)ruthenium(II)] :-

As for the chloro complex but using $RuBr_2(PPh_3)_4$ (0.2g) and diethylphenylphosphine (0.16 cm^3). The orange-red crystals separated from the hot reaction mixture and were purified above (0.05g: 48%) m.p. 158-159°C [Found: C, 47.2; H, 6.0; M(in C_6H_6) 1348. Calc. for $C_{50}H_{75}Br_4P_5Ru_2$: C, 44.4; H, 5.5% M 1352]. Again the high analyses figures are ascribed to the presence of solvent of crystallisation since the ^{31}P nmr spectrum (see text) indicated the dimeric formulation. I.r. (mull 2000-400 cm^{-1}) - identical to that of $Ru_2Cl_4(PEt_2Ph)_5$.

Tri-μ-chloro[tris(chlorodiphenylphosphine)ruthenium(II)][chloro bis-(chlorodiphenylphosphine)ruthenium(II)] :-

$RuCl_2(PPh_3)_4$ (0.40g) in degassed hexane (50 cm^3) was treated with chlorodiphenylphosphine (0.40 cm^3) and the mixture refluxed for three hours under nitrogen. The complex was filtered off as a bright yellow powder and washed thoroughly with light petroleum (bp 40 - 60°C) (0.14g; 60%) m.p. 191-193°C. [Found: C, 51.2; H, 3.7; Cl, 21.2. Calc. for $C_{60}H_{50}Cl_9P_5Ru_2$: C, 49.8; H, 3.5; Cl, 22.0%]

Dichlorotetrakis(methyldiphenylphosphine)ruthenium(II)

$RuCl_2(PPh_3)_4$ (0.4g) and methyldiphenylphosphine (0.4 cm^3) were refluxed in n-hexane (60 cm^3) under nitrogen for 1 hour. The resulting green solution was filtered hot, and then evaporated until precipitation began. The precipitate was filtered† and extracted into hexane. The

†Further concentration of this filtrate yields more of the complex which can then be purified as described.

extractions (golden yellow solution) were evaporated to small volume to precipitate the orange crystals of the complex which were filtered and dried in vacuo at 40°C (0.14g; 45%) m.p. 129 - 133°C (decomp 110°C) [Found:- C, 63.6; H, 5.4; Cl, 7.2. Calc. for $C_{52}H_{52}Cl_2P_4$ Ru:- C, 64.2; H, 5.4; Cl, 7.3%] I.r. (mull -2000-400 cm^{-1}) 1628vw, 1584w, 1570w, 1490sh, 1484m, 1433s, 1425sh, 1382m, 1369sh, 1278m, 1272sh, 1261sh, 1199sh, 1189w, 1158m, 1092m, 1080shbr, 1029w, 100w, 928sh, 919w, 902sh, 900sh, 893sh, 888s, 873sh, 850w, 838w, 750sh, 740s, 720m, 713sh, 700sh, 691s, 678sh, 668sh, 618w, 522sh, 508s, 498m, 489sh, 450m, 437m, 402m.

Dibromotetrakis(methyldiphenylphosphine)ruthenium(II):-

As for the chloro complex but using $RuBr_2(PPh_3)_4$ (0.3g) and methyldiphenylphosphine (0.3 cm^3) to give the orange complex (0.06g; 29%) m.p. 132 - 5°C (decomp). [Found: C, 58.8; H, 5.0. Calc. for $C_{52}H_{52}Br_2P_4Ru$:- C, 58.8; H, 4.9%] I.r. (mull -2000-400 cm^{-1}) -identical to that of $RuCl_2(PMePh_2)_4$.

Dichlorotetrakis(dimethylphenylphosphine)ruthenium(II):-

$RuCl_2(PPh_3)_4$ (0.4g) and dimethylphenylphosphine (0.3 cm^3) were refluxed in light petroleum (bp 60 - 80°C) (70 cm^3) under nitrogen, for three hours. The yellow crystals of the product were filtered from the hot solution and washed thoroughly with light petroleum (bp 40 - 60°C) to remove excess phosphine (0.16g; 65%) m.p. 165 - 170°C (decomp) [Found:- C, 53.1; H, 5.6; Cl, 9.7. Calc. for $C_{32}H_{44}Cl_2P_4Ru$:- C, 53.0; H, 6.1; Cl, 9.8%] I.r. (mull -2000-400 cm^{-1}) 1582w, 1570w, 1480m, 1476sh, 1432s, 1420sh, 1399w, 1378m, 1367sh, 1321m, 1313w, 1289m, 1277sh, 1271m, 1185m, 1158w, 1091m and br, 1077w, 1024w, 1001w, 991vw, 978w, 940s and br, 910s and br, 874w, 855w, 842m, 750w, 722s, 707s, 696sh, 673s, 669sh, 620w, 500s, 431sh, 427s, 402m.

Dibromotetrakis(dimethylphenylphosphine)ruthenium(II):-

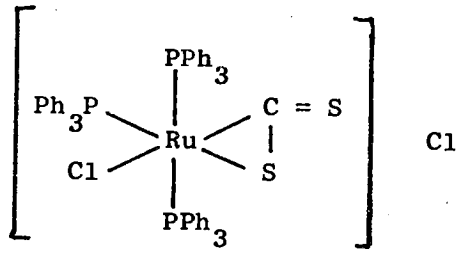
As for the chloro complex using $RuBr_2(PPh_3)_4$ (0.20g) and dimethylphenylphosphine (0.13 cm^3) to give a yellow complex (0.055g; 41%) m.p. 144 - 160°C (decomp) [Found:- C, 47.6; H, 5.6. Calc. for $C_{32}H_{44}Br_2P_4Ru$: C, 47.2; H, 5.4%] I.r. (mull -2000-400 cm^{-1}) -identical to that of $[RuCl_2(PMe_2Ph)_4]$.

CHAPTER THREE

REARRANGEMENT REACTIONS OF SOME RUTHENIUM(II) THIOCARBONYL TRIPHENYLPHOSPHINE COMPLEXES

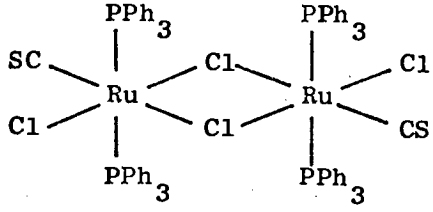
3.1 Introduction

It has been reported[178] that when $RuCl_2(PPh_3)_3$ is refluxed in carbon disulphide under nitrogen for five minutes, a deep red solution is obtained which on cooling and filtration gave a small amount of the dark red crystalline solid $[RuCl(\eta CS_2)(PPh_3)_3]Cl$ (L)† (νCS_2; 1105s, 1055s, 850m. cm^{-1})($\nu RuCl$; 330 m. cm^{-1})(νRuS; 265m. cm^{-1})

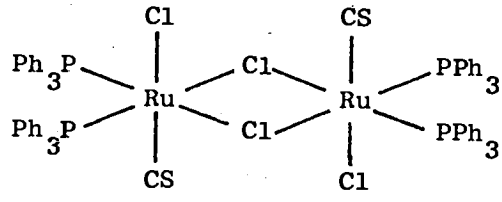


(L)

When the filtrate was concentrated and diethylether was added, the red complex $[RuCl_2(CS)(PPh_3)_2]_2$ (LI) (νCS; 1290s. cm^{-1}) was precipitated. The far infra-red spectrum showed the presence of both bridging ($\nu RuCl$: 250 cm^{-1}) and terminal ($\nu RuCl$; 318, 268 cm^{-1}) chloride groups, supporting a formulation such as (LIa) or (LIb).



(LIa)



(LIb)

This complex readily undergoes bridge cleavage reactions with carbon monoxide and pyridine to give monomeric complexes of the type $RuCl_2(CS)(PPh_3)_2L$ (L = CO, pyridine).[178]

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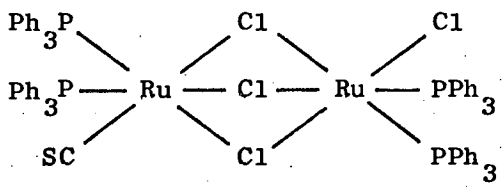
†Very recent work[186] suggests that this complex should be reformulated as containing the $Ph_3\overset{+}{P}\text{-}\overset{-}{C}S_2$ ligand and not as a ηCS_2 complex.

The reaction between $RuCl_2(PPh_3)_3$ and CS_2 was repeated by Switkes who used cleavage reactions of such double halide bridged species as a general method of preparation of ruthenium(II) anions.[179]

However, the reaction afforded a consistently low yield of (LI) (ca. 16% versus 70% in ref.(178)). Thus, most of the solvent was removed from the red ethereal solution and excess light petroleum (bp 60 - 80°C) added. A pinkish-red precipitate (LII) was obtained (ca. 40% yield). When the red ethereal solution was left to stand for ca. 15 mins., the same complex (LII) was obtained as maroon-red crystals. Both of these samples were then insoluble in diethylether.

The physical data for (LI) and (LII) appeared identical at first sight. Thus, both complexes are diamagnetic, non-conducting in dichloromethane solution, completely soluble in benzene, chloroform and dichloromethane; both analyse closely (C, H, P and Cl) for "$RuCl_2(CS)(PPh_3)_2$" (see experimental section) and molecular weight determinations show that both complexes are dimeric in benzene. There are however, slight differences in the melting points ((LI) 165 - 6°C (decomp); (LII) 167 - 8°C), the far infra-red spectra (see table 3:1) and in the position of νCS ((LI) 1290 cm^{-1}; (LII) 1284 cm^{-1}). Furthermore, although (LI) is completely soluble in acetone, (LII) is only transiently so and rapidly precipitates from solution as an acetone solvate (νCO 1705; νCC 1221 cm^{-1}). Sulphur analyses on (LII) were consistently 50% less than those of (LI).

By means of the liquid diffusion method[180] using a dichloromethane/acetone solvent mixture, crystals of (LII) were obtained suitable for X-ray analysis,[181] which established the structure of (LII) as containing a triple halide bridge with one CS group per dimer.



(LII)

As the overall packing in the crystal is governed by the triphenylphosphine groups, disorder arises in the crystal as the two orientations of the molecule (that shown in (LII) and the one where the chloro and thiocarbonyl groups are interchanged) are virtually indistinguishable for packing considerations. This leads to some uncertainty in the length of the bonds from ruthenium to the terminal chloro and thiocarbonyl groupings.

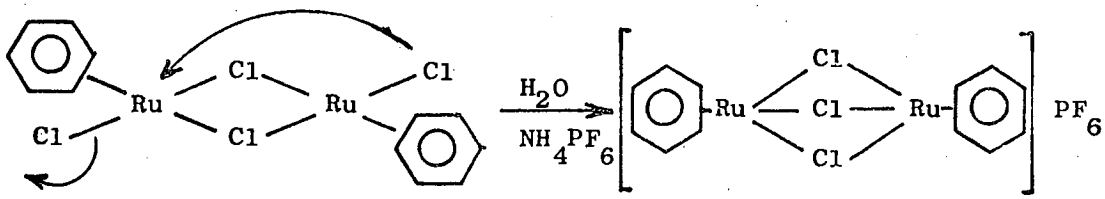
It is interesting to note that the mean value of the Ru-Cl bridged distances (2.51Å) is marginally but significantly greater than those determined for other triple chloride bridged complexes of ruthenium; $[(CO)_2(SnCl_3)RuCl_3Ru(CO)_3]$ 2.43Å;[182] $[(PBu_3)_2ClRuCl_3RuCl(PBu_3)_2]$ 2.44Å;[125] $[(PEt_2Ph)_2ClRuCl_3Ru(PEt_2Ph)_3]$ 2.46Å.[183] The recently reported complex $[(PPh_3)_2ClRuCl_3Ru(N_2)(PPh_3)_2]$ made from $RuCl_2(PPh_3)_4$ and molecular nitrogen by the novel technique of reverse osmosis[184] is analogous to (LII) and it would be expected that it would exhibit identical packing behaviour, producing similar disorder in the crystal.

3.2 Results and Discussion

When $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ is treated with $NaBPh_4$ in ethanol, rearrangement to the triple chloride bridged cation $[(\eta^5\text{-}C_5Me_5)_2Rh_2Cl_3]BPh_4$ occurs.[169] Similarly, by reacting $[IrHCl(SPh)(PPh_3)_2]_2$ with $AgClO_4$ in acetone the triple bridged $[(PPh_3)_2HIr(SPh)_2ClIrH(PPh_3)_2]ClO_4$ is obtained[185] and $[RuCl_2(arene)]_2$ when treated with NH_4PF_6 in water

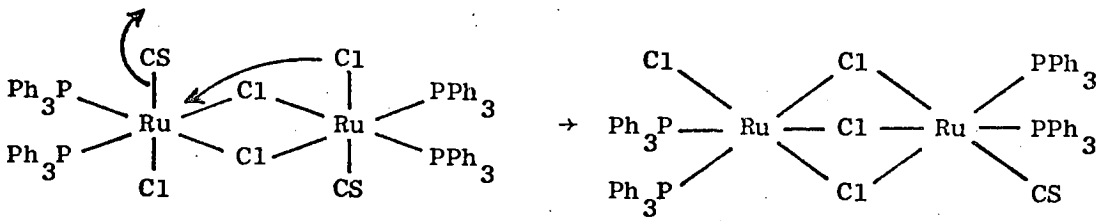
produces $[Ru_2Cl_3(arene)_2]PF_6$ (arene = benzene or p-cymene).[170]

The suggested mechanism for these rearrangements is by intramolecular displacement of a chloride ion e.g.:-



$+ NH_4Cl$ . . . (21)

Such a mechanism could also be employed to account for the formation of (LII) from (LI) via an intramolecular displacement of a thiocarbonyl group:-



+CS . . . (22)

Thus a careful investigation of the reaction of $RuCl_2(PPh_3)_3$ in CS_2 was performed and the products re-examined by infra-red and ^{31}P nmr spectroscopy in an attempt to elucidate the reaction mechanism.

Samples of (LI) and (LII) were prepared as described previously (see experimental section for detail of preparations) and their ^{31}P nmr spectra were measured.

The ^{31}P nmr spectrum of $[RuCl_2(CS)(PPh_3)_2]_2$ in C_6H_6/C_6D_6 at ambient temperature exhibits two resonances at 31.3 and 24.4 ppm. The former disappears when the solution is left for several days. In $CDCl_3$ two resonances are also observed at 31.8 and 29.1 ppm and in addition extra resonances are seen to grow at 48.1 and 37.6 ppm. The resonances at 24.4 ppm (benzene) and 29.1 ppm (chloroform) may

be attributed to $OPPh_3$ indicating the instability of solutions of (LI) relative to aerial oxidation. The singlet at 31 ppm is attributed to $[RuCl_2(CS)(PPh_3)_2]_2$ and is consistent with either of the isomers (LIa) or (LIb)

Consistent with the x-ray determination, the ^{31}P nmr of the complex $Ru_2Cl_4(CS)(PPh_3)_4$ in C_6H_6/C_6D_6 solution exhibits two AB quartets centred at 48.8 ppm (J_{AB}= 38.1Hz; δ_{AB} = 124.9Hz) and 35.2 (J_{AB}= 24.4Hz; δ_{AB} = 43.8Hz). (fig. 19) In $CDCl_3$ solution the quartets are centred at 48.3 ppm (J_{AB}= 37.4Hz; δ_{AB} = 94.0Hz) and 36.1 ppm (J_{AB}= 24.6Hz; δ_{AB} = 54.9Hz); a weak singlet at ca 29 ppm ($OPPh_3$) is also present. The similarity in position of the lower frequency quartet in (LII) with the strong singlet of (LI) in $CDCl_3$, together with the greater shielding effect of Cl relative to CS, suggests that this quartet arises from the PPh_3 groups cis- to the thiocarbonyl group.

A study of the relative yields of $[RuCl_2(CS)(PPh_3)_2]_2$ and $Ru_2Cl_4(CS)(PPh_3)_4$ as a function of reaction time, would at first sight appear to support the hypothesis (eqn. (22)). Thus, increasing the time of reaction from 2 mins. to 60 mins. increases the yield of (LII) and decreases the amount of (LI) (see experimental section). However further experiments show that on refluxing (LI) in CS_2 for up to 10 hours, none of the triply bridged species is produced. Similarly, there is no evidence for the conversion of $[RuCl_2(CS)(PPh_3)_2]_2$ to $Ru_2Cl_4(CS)(PPh_3)_4$ in acetone, benzene or chloroform solutions.

However, as has been observed previously,[179] when (LI) is shaken in degassed acetone for several days, a very small quantity of golden yellow crystals is deposited. The i.r. spectrum of this material shows evidence of solvent acetone, thiocarbonyl (νCS 1300 cm^{-1})

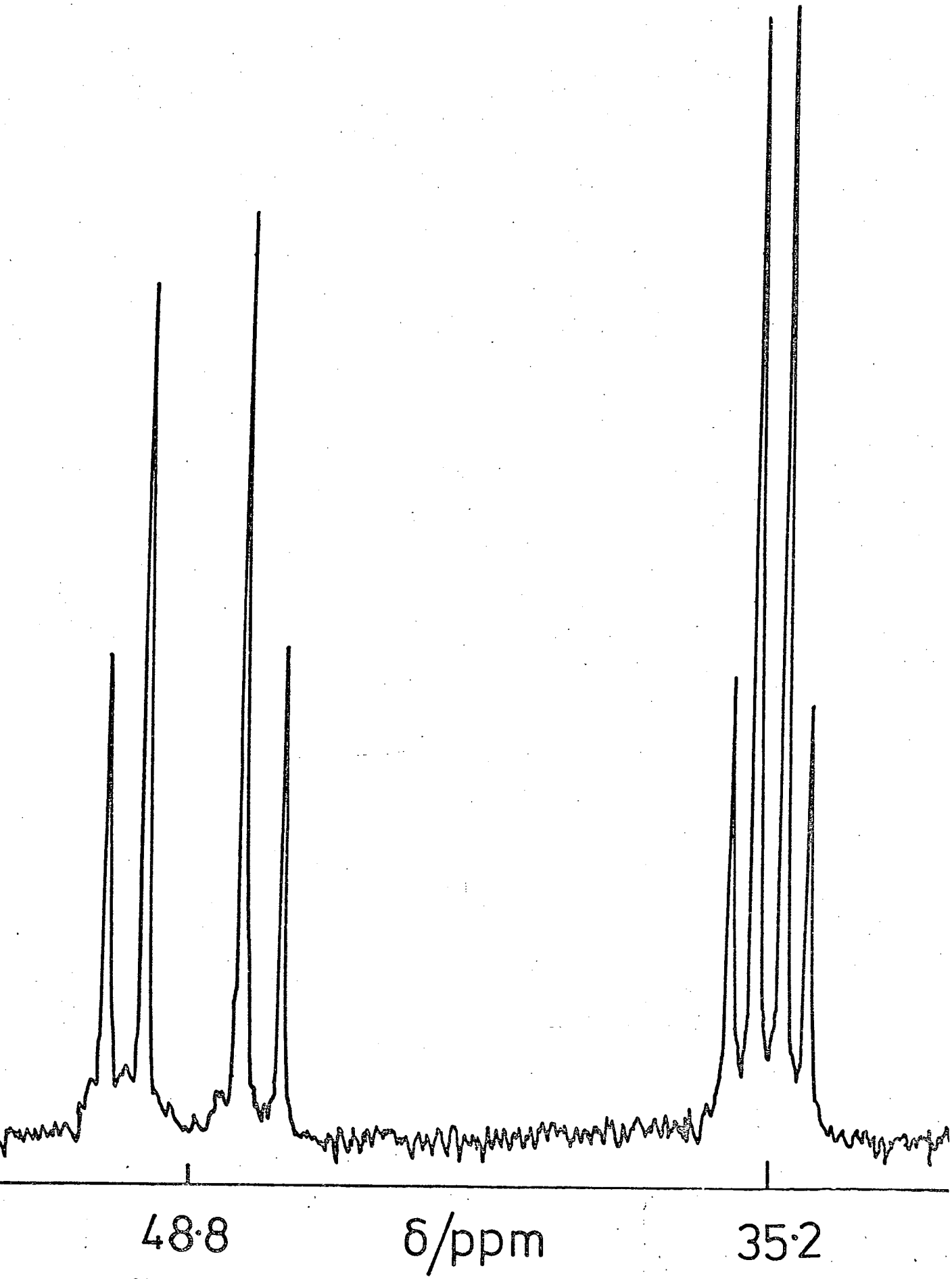
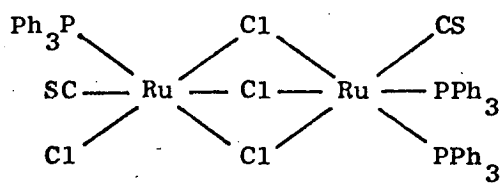


Figure 19 ^{31}P nmr spectrum of $Ru_2Cl_4(CS)(PPh_3)_4$ in benzene at ca 298K.

and triphenylphosphine. The far i.r. spectrum (see table 3:1) has bands at 326, 288 and 259 cm^{-1} which indicate both terminal and bridging chloro groups, and the compound is diamagnetic (Evans' Method [187]). The formulation proposed on the basis of this and analytical evidence is $[(PPh_3)(CS)ClRuCl_3Ru(CS)(PPh_3)_2]$ acetone (LIII).

The ^{31}P nmr spectrum of (LIII) in $CDCl_3$ at 308K consists of two strong resonances at 48.1 and 37.7 (broad) ppm (relative intensity 1:2 and two other much weaker resonances at 50.2 and 35.5 ppm relative intensity 1:2. This spectrum may be interpreted in terms of a mixture of the isomeric forms of the complex (LIII) (see chapter 4) although it is not possible to make definite assignments of the observed resonances to the various isomers involved due to the broad nature of the spectra.



(LIII)

Furthermore, in the ^{31}P nmr spectrum in $CDCl_3$ of (LI) weak resonances were observed at 48.1 and 37.6 ppm (see earlier) which correspond to one set of resonances observed in the spectrum of (LIII). Thus the formation of $Ru_2Cl_4(CS)_2(PPh_3)_3$ from $[RuCl_2(CS)(PPh_3)_2]_2$ could be explained in terms of an intramolecular rearrangement of the type shown in equation (22) except that the reaction would involve displacement of a PPh_3 group (rather than a CS group) by the chloride ion. (This type of complex and the isomers involved will be discussed fully in Chapter 4).

At this juncture, it must be concluded that $Ru_2Cl_4(CS)(PPh_3)_4$ is not in fact formed from $[RuCl_2(CS)(PPh_3)_2]_2$ and that both (LI) and (LII) are probably formed by competing reactions from $RuCl_2(PPh_3)_3$ or $[RuCl(\eta CS_2)(PPh_3)_3]Cl$.

Such a mechanism might involve a five coordinate species of the type "$RuCl_2(CS)(PPh_3)_2$" (LIV) which could be formed by elimination of Ph_3PS from the cationic complex (L) (scheme 3:1 step (iv)) or by direct reaction of $RuCl_2(PPh_3)_3$ with carbon disulphide. The latter might form a complex of the type (LV) (step (i)) involving a coordinated CS_2 group, which may then react further to form the species $[RuCl(CS_2)(PPh_3)_3]Cl$(L) (step (ii)) or eliminate $SPPh_3$ to produce the five coordinate "$RuCl_2(CS)(PPh_3)_2$" (step (iii)).

This coordinatively unsaturated species might then undergo dimerisation to give the double halide bridged complex (LI) (step vi) or combine with unreacted $RuCl_2(PPh_3)_3$ to give the triple halide bridged complex (LII) (step (v)).

It is also probable therefore that the formation of the complex $Ru_2Cl_4(CS)_2(PPh_3)_3$ (LIII) does not take place from (LI) via an intramolecular displacement of phosphine but rather by, firstly solvent assisted bridge cleavage of (LI) (reverse of step (vi)) followed by dimerisation with elimination of PPh_3(step (viii)).†

Attempts to produce a cationic complex of the type $[(PPh_3)_2(CS)RuCl_3Ru(CS)(PPh_3)_2]Cl$ (by means of an intramolecular displacement of chloride ion) by treating solutions of (LI) with $NaBPh_4$ produced only intractable black residues. However, recent work

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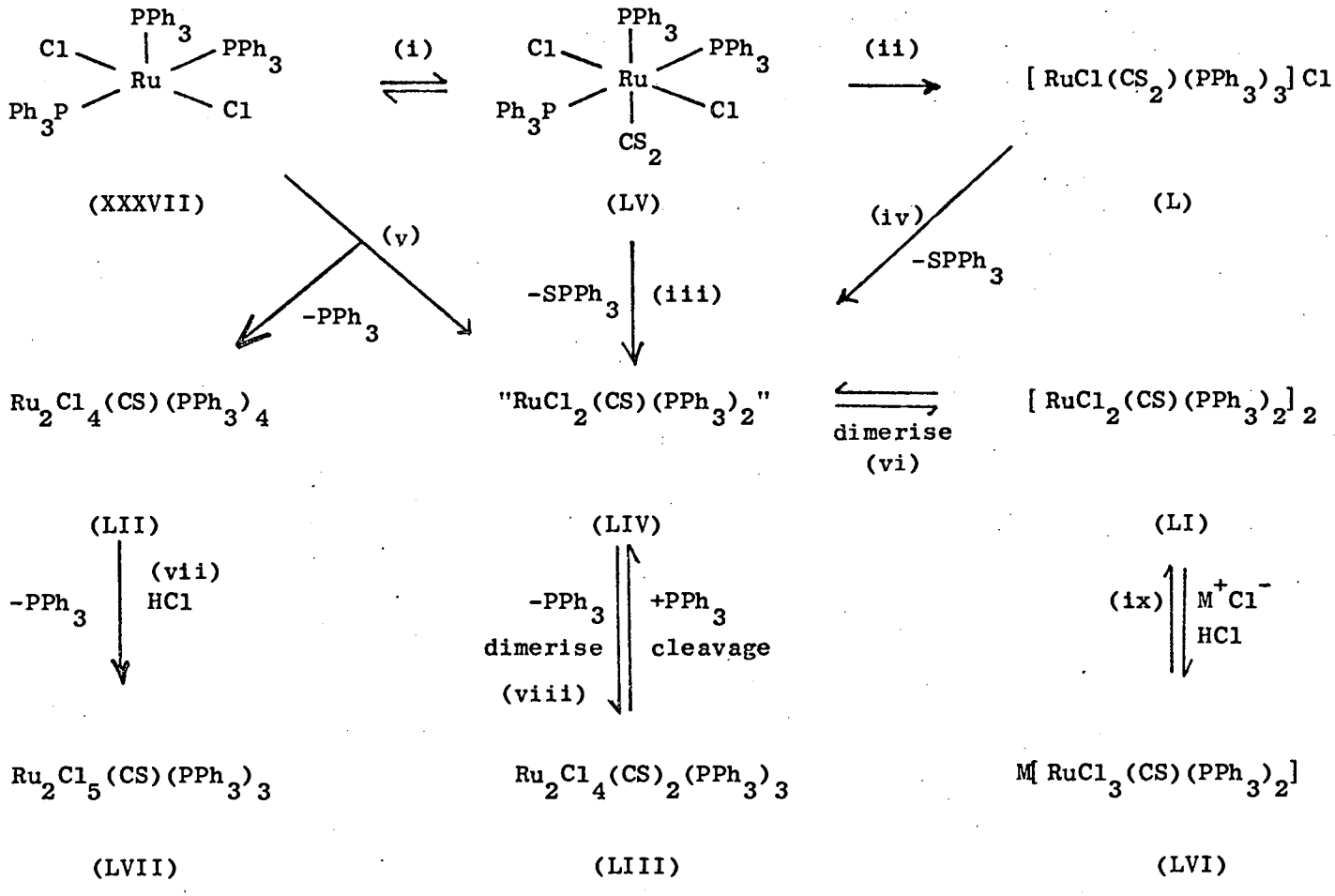
†Recent studies[171,188] involving $[RuCl_2(CS)(PPh_3)_2dmf]$ support this mechanism.

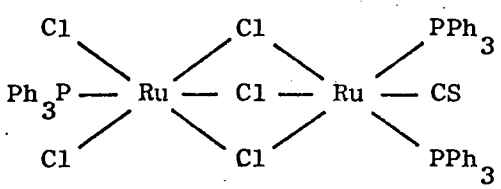

PPh3
Cl
Ru
PPh3
Ph3P
Cl
(i)
CS2
(ii)
[RuCl(CS2)(PPh3)3]Cl
(XXXVII)
(LV)
(L)
(v)
-PPh3
-SPPh3
(iii)
(iv)
-SPPh3
Ru2Cl4(CS)(PPh3)4
"RuCl2(CS)(PPh3)2"
dimerise
(vi)
[RuCl2(CS)(PPh3)2]2
(LII)
(LIV)
(LI)
-PPh3
(vii)
HCl
-PPh3
dimerise
(viii)
+PPh3
cleavage
(ix)
M+Cl-
HCl
Ru2Cl5(CS)(PPh3)3
Ru2Cl4(CS)2(PPh3)3
M[RuCl3(CS)(PPh3)2]
(LVII)
(LIII)
(LVI)

SCHEME 3.1

has shown that when $Ru_2Cl_4(CS)_2(PPh_3)_3$(LIII) is treated with $NaPBh_4$ and PPh_3 in dichloromethane the orange-yellow $[(PPh_3)_2(CS)RuCl_3Ru(CS)(PPh_3)_2]BPh_4$ may be isolated.(188)

When $[RuCl_2(CS)(PPh_3)_2]_2$ was shaken with excess of $Ph_4AsCl.HCl$ in degassed acetone under nitrogen for several days,(179) slow conversion to the red crystalline $Ph_4As[RuCl_3(CS)(PPh_3)_2].2$ acetone (LVI) (νCS 1272 cm^{-1}; νRuCl 320 cm^{-1}) occurred. The same anion was obtained by using either triphenylbenzylphosphonium chloride or tetraethylammonium chloride in the presence of concentrated hydrochloric acid (step (ix)).

However, the triple halide bridge of the complex $Ru_2Cl_4(CS)-(PPh_3)_4$ is not cleaved under these conditions to give a ruthenium(II) anionic complex. It does however react slowly in acetone with concentrated hydrochloric acid to give a sparingly soluble orange brown solid. This material is sharp melting (234°C), non conducting in dichloromethane and its infra-red spectrum is very similar to (LII) except that it has two thiocarbonyl bands (νCS 1303, 1297 cm^{-1}) and there are slight differences in the far i.r. region. The complex is paramagnetic giving strong e.s.r. (electron spin resonance) signals (g_1 2.43; g_2 1.75) and analyses closely (C,H,Cl) for $[(PPh_3)Cl_2Ru-Cl_3Ru(CS)(PPh_3)_2]$. 2 acetone.



(LVII)

This formulation is supported by the magnetic moment of 2.00 B.M. per dimer obtained on a Faraday balance at 292K (c.f. $[(PBu_3)_2ClRuCl_3Ru-Cl(PBu_3)_2]$ with μeff = 1.50 B.M. per dimer)(123) and the formation of

(LVII) from (LII) is readily explained by invoking an intermolecular displacement of a PPh_3 group by a chloride ion (step (vii)).

3.3 Conclusions

It would appear for these thiocarbonyl complexes that, as with the tertiary phosphine complexes (chapter 2), formation of triple bridged species does not occur by intramolecular displacement via a double halide bridged intermediate but rather by direct dimerisation. The latter mechanism is more reasonable than the former since six coordinate d^6 compounds are generally kinetically inert.

On the basis of these observations it is probable that the "conversion" of other double bridged complexes (e.g. $[RhCl_2(C_5Me_5)]_2$, $[RuCl_2(arene)]_2$, $[IrHCl(SPh)(PPh_3)_2]_2$) to triple bridged complexes, occurs by means of a bridge cleavage, ligand dissociation, dimerisation mechanism similar to that proposed for $[RuCl_2(CS)(PPh_3)_2]_2$. Recent work[189] with $[RuCl_2(arene)]_2$ supports this general mechanism.

TABLE 3:1

Far infra-red spectra (400 - 250 cm^{-1}) of some ruthenium(II) triphenylphosphine complexes containing CS or CS_2.

Compound	Bands cm^{-1}
$[RuCl(\eta CS_2)(PPh_3)_3]Cl$ (L)	330 cm^{-1} (m) 265 cm^{-1} m
$[RuCl_2(CS)(PPh_3)_2]_2$ (LI)	330-320 (m), 260 w
$[Ru_2Cl_4(CS)(PPh_3)_4]$ (LII)	318 (s), 308 (m,sh), 260 (m)
$[Ru_2Cl_4(CS)_2(PPh_3)_3]$ (LIII)	326 (s), 288 (s), 259 (m)
$[Ru_2Cl_5(CS)(PPh_3)_3]$ (LVII)	339 (vs), 286 (m), 260 (m)

3.4 Experimental

Physical measurements were as described in chapter 2. In addition magnetic susceptibilities were measured by the Faraday method (solid) and the Evans' nmr method (solution).[187] Esr spectra were measured on a Decca X-1 spectrometer operating at 9.27GHz with a 100kHz magnetic field modulation using D.P.P.H. (diphenylpicrylhydrazyl) as reference.

Reaction of Dichlorotris(triphenylphosphine) ruthenium(II) with carbon disulphide:-

$RuCl_2(PPh_3)_3$ (0.19g) was refluxed for 5m in degassed CS_2 (30 cm^3) under an atmosphere of nitrogen. The solution was then cooled in ice in a stream of nitrogen. Filtration of the deep-red solution gave a red crystalline residue (0.016g; 8%) m.p. 175-176°C. This material initially contains some CS_2 of solvation (ν_{CS_2}, 1515 cm^{-1}) but this is removed by gentle suction. The product is then identical (i.r. spectrum and analysis) to that reported earlier[178] ie $[RuCl(\eta CS_2)(PPh_3)_3]Cl$ [Found, C, 64.0; H, 4.2% Calc. for $C_{55}H_{45}Cl_2RuP_3S_2$:- C, 63.8; H, 4.4%].

The remaining red solution was concentrated on a rotary evaporator to ca 5 cm^3 volume and then treated with excess diethyl ether giving a microcrystalline purple-red solid and a red solution. The solid was shaken with degassed acetone for ca 10m, (virtually all soluble) filtered and the solvent removed. The residue was redissolved in degassed benzene leaving a small undissolved amount of $[RuCl(\eta CS_2)(PPh_3)_3]Cl$ (i.r. evidence). Removal of benzene, followed by washing with diethyl ether then gave Di-μ-chloro[chloro (thiocarbonyl)bis (triphenylphosphine)ruthenium(II)][chloro(thiocarbonyl) bis(triphenylphosphine)ruthenium(II)] (0.024g; 16%) m.p. 165-166°C (decomp) ν_{CS} 1290 cm^{-1} [Found:- C, 60.3; H, 4.2; Cl, 9.3; P, 8.7;

S, 4.2%M(C_6H_6)974. Calc. for $C_{74}H_{60}Cl_4P_4Ru_2S_2$:- C, 60.0; H, 4.1; Cl, 9.5; P, 8.4; S, 4.3% M, 1480]. This compound is completely soluble in benzene, dichloromethane, chloroform and acetone but rapidly oxidises in the latter giving a greenish-brown solution. As reported earlier,[178] it appears stable to oxidation in the other solvents. The compound is non-conducting in dichloromethane and diamagnetic.

Removing the diethyl ether immediately from the remaining red solution and then adding excess light petroleum (bp 60-80°C) gave a further pinkish-red precipitate which, after washing well with acetone to remove any $[RuCl_2(CS)(PPh_3)_2]_2$, left Tri-μ-chloro[chlorobis(triphenylphosphine)ruthenium(II)][(thiocarbonyl) bis (triphenylphosphine)ruthenium (II)] (0.057g; 39%) m.p. 167-168°C ν_{CS} 1284 cm^{-1} [Found:- C, 60.7; H, 4.3; Cl, 9.4; P, 8.5; S, 2.3% M (C_6H_6) 1423. $C_{73}H_{60}Cl_4P_4Ru_2S$ requires C, 61.0: H, 4.2; Cl, 9.9; P, 8.6; S, 2.2% M, 1436]. The same compound separated out in smaller yield when the diethylether solution was left to stand for a few minutes. This compound is also completely soluble in benzene, dichloromethane and chloroform but only slightly soluble in acetone. Although the compound is quite stable in acetone suspension, it is rapidly oxidised in benzene and the other solvents. The compound is non-conducting (CH_2Cl_2) and diamagnetic.

The same products are also obtained by treating the initial CS_2 solution (after filtering off $[RuCl(CS_2)(PPh_3)_3]Cl$) with light petroleum (bp. 60-80°C). In this instance, both thiocarbonyl compounds are immediately precipitated and can be separated by shaking with degassed acetone for 10-15 m. Under these conditions, $(PPh_3)_2ClRuCl_3$-$Ru(CS)PPh_3)_2$ separates out with an acetone of solvation (ν_{CO} 1705 cm^{-1}; which can be removed by prolonged pumping at room temperature.

Finally, the relative percentages of $[RuCl(CS_2)(PPh_3)_3]Cl$, $[RuCl_2CS(PPh_3)_2]_2$ and $(PPh_3)_2ClRuCl_3Ru(CS)(PPh_3)_2$ appear to depend on the time of reaction. Thus, after only 2m, percentage yields are 5, 24 and 50%, after 5 mins 8, 16 and 39% and after 60 mins 11,9 and 47% respectively. This indicates that the yields of η- CS_2 and mono-CS compounds increase with time whereas that of the bis-CS compound decreases with time.

Tri-μ-chloro[chloro(thiocarbonyl)(triphenylphosphine)ruthenium(II)] [(thiocarbonyl)bis(triphenylphosphine)ruthenium(II)] acetone(1/1):-

$[RuCl_2(CS)(PPh_3)_2]_2$ was shaken in degassed acetone for several days to give a very small amount of golden-yellow crystals m.p. 264°C (ν_{CS} 1300 cm^{-1}; ν_{CO} 1708 cm^{-1}) [Found:- C, 53.5; H, 3.7%, $C_{59}H_{51}Cl_4OP_3Ru_2S_2$ requires C, 52.5; H, 3.7%] ^{1}H nmr spectrum ($CDCl_3$) δ 7.2 (phenyl); δ 2.1 (acetone).

Tri-μ-chloro[(thiocarbonyl)bis(triphenylphosphine)ruthenium(II)] [dichloro(triphenylphosphine)ruthenium(III)] acetone (1/2):-

$(PPh_3)_2ClRuCl_3Ru(CS)(PPh_3)_2$ (acetone) (0.12g) was suspended in degassed acetone (18 cm^3) and shaken with concentrated hydrochloric acid (3.0 cm^3) for several days. The orange-brown solid was then filtered off and washed with water, acetone and light petroleum (bp 60 - 80°C) (0.07g; 66%) mp. 234°C ν_{CS} 1303, 1297 cm^{-1}; ν_{CO} 1710 cm^{-1}, ν_{CC} 1223 cm^{-1} [Found: C, 55.2; H, 4.2; Cl, 12.8% $C_{61}H_{57}Cl_5O_2P_3Ru_2S$ requires C, 55.2; H, 4.3; Cl, 13.4%]. The compound is sparingly soluble in CH_2Cl_2, non-conducting, gives strong esr signals (g_1, 2.43; g_2, 1.75; the complex is axially symmetric) and has a magnetic moment of 2.00 BM per dimer at 292K (solid).

The same compound is obtained using a mixture of $Ph_4AsCl.HCl$ and HCl.

CHAPTER FOUR

REARRANGEMENT REACTIONS OF SOME RUTHENIUM(II) CARBONYL TRIPHENYLPHOSPHINE COMPLEXES

4.1 Introduction

In Chapter 3 the reaction of $RuCl_2(PPh_3)_3$ and carbon disulphide has been shown to give the thiocarbonyl complexes (LI) and (LII) and an overall mechanism (scheme 3:1) for their formation and rearrangement proposed. Although this mechanism was difficult to verify for the thiocarbonyl compounds, due to the non-availability of a five coordinate thiocarbonyl complex (LIV)†, the feasibility of this mechanism may be verified by the synthesis of the corresponding carbonyl complexes by this method.

Recently, the preparation of $RuCl_2(CO)(PPh_3)_2S$ (S = N, N'-dimethylformamide)(ν_{CO} 1911 cm^{-1}; ν_{CO}, dmf., 1630 cm^{-1}) by reaction of a suspension of $RuCl_2(PPh_3)_3$ in dmf. with carbon monoxide for a few minutes at 298K, has been described.(190) It was reported that this compound when recrystallised from a mixture of methanol and dichloromethane gave the five coordinate complex "$RuCl_2(CO)(PPh_3)_2$".†† This complex has been shown to be a six coordinate methanolate $RuCl_2(CO)(PPh_3)_2MeOH$ (ν_{CO} 1931, 1921 cm^{-1}; ν_{OH}, MeOH, 3480 cm^{-1}).(191)

However, as these complexes would be expected to lose their coordinated solvent molecules readily when dissolved in less polar

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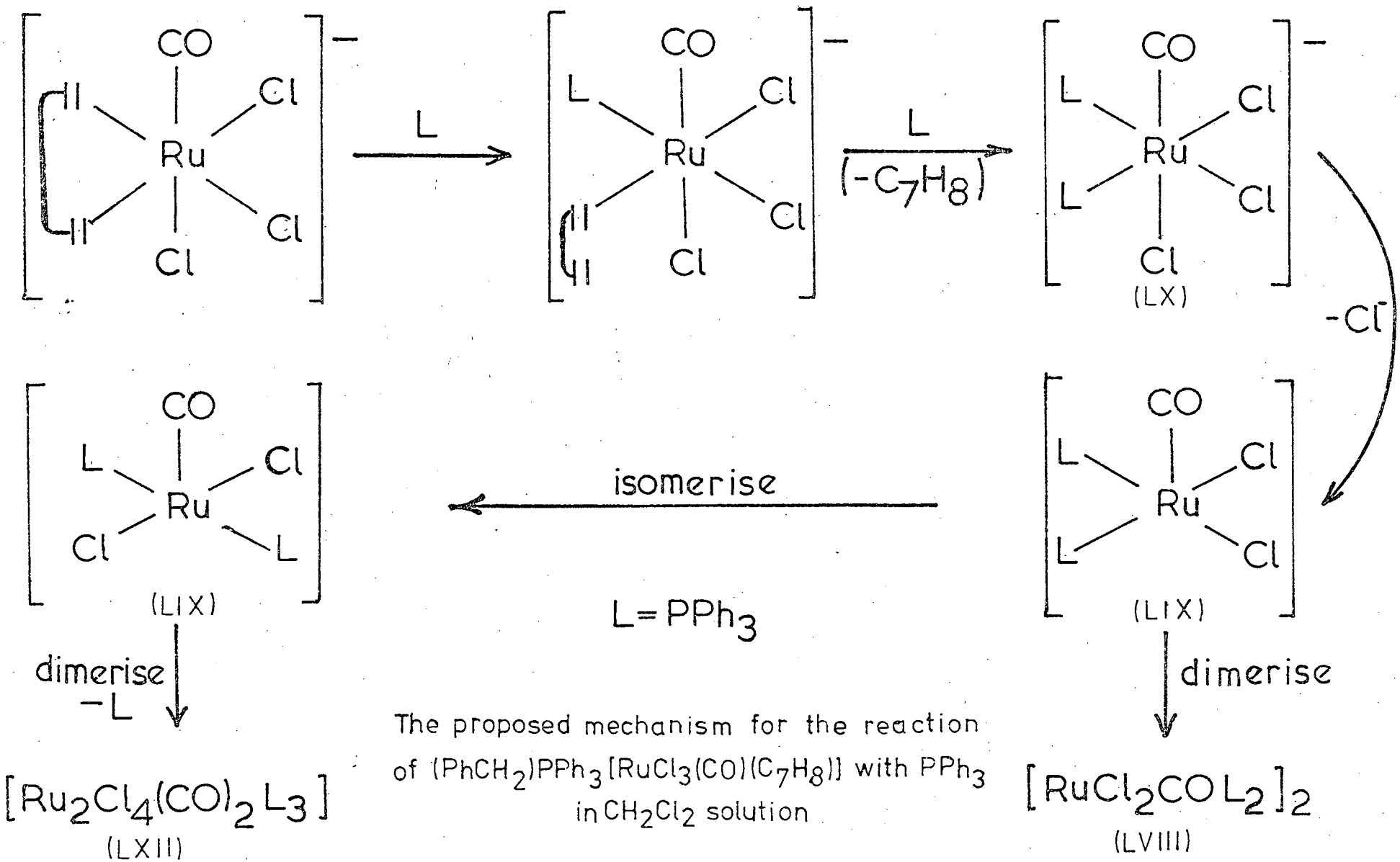
†Very recently such a complex has been prepared and used to verify the mechanism for the thiocarbonyl system.(171,188)

††The same formulation has been proposed for the dark red-brown solid (ν_{CO} 1978, 1960 sh cm^{-1}) obtained from reaction of $RuCl_3.3H_2O$ with PPh_3 in 2-ethoxyethanol, isoamylalcohol or n-butanol.(115) It is more likely that this compound is in fact a dimer, possibly some form of triple bridged species formed by combination of the carbonyl species with $RuCl_2(PPh_3)_3$ or $RuCl_3(PPh_3)_2S$.



The proposed mechanism for the reaction of $(PhCH_2)PPh_3[RuCl_3(CO)(C_7H_8)]$ with PPh_3 in CH_2Cl_2 solution

Scheme 4-1

solvents such as dichloromethane, thus generating a five coordinate intermediate analogous to that postulated for the thiocarbonyl system, they provide an excellent method of verifying the mechanism.

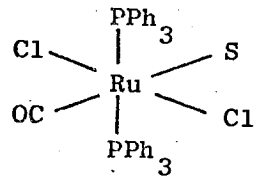
Thus, if the proposed mechanism is valid, refluxing $RuCl_2(CO)(PPh_3)_2S$ in CH_2Cl_2 should produce the corresponding double halide bridged complex $[RuCl_2(CO)(PPh_3)_2]_2$ (scheme 3:1 step (vi)) and/or the complex $Ru_2Cl_4(CO)_2(PPh_3)_3$ with elimination of a phosphine group (step (viii)). Similarly, reaction of equimolar ratios of $RuCl_2(CO)(PPh_3)_2S$ and $RuCl_2(PPh_3)_3$ should give the tri-μ-chloro complex analogous to (LII) (Step (V)).

The double chloride bridged complex $[RuCl_2(CO)(PPh_3)_2]_2$ (ν_{CO} 2029m, 1993s, 1906s cm^{-1}) (LVIII) has been prepared previously from the reaction of $(PhCH_2)PPh_3[RuCl_3(CO)(C_7H_8)]$ with a 1:2 molar ratio of triphenylphosphine in dichloromethane solution.[188,191] The proposed mechanism for this reaction (Scheme 4:1) also involves the dimersation of the five coordinate monomeric complex "$RuCl_2(CO)(PPh_3)_2$" (LIX) formed by loss of a chloride ion from the anionic $[RuCl_3(CO)(PPh_3)_2]^-$ (LX). The ^{31}P nmr spectrum of this complex (LVIII) in $CDCl_3$ at 303K comprises mainly two singlets at 17.2 and 25.5 ppm, assigned to isomers of (LVIII). Weak multiplets are also observed at 38.5, 42.3 and 52.6 ppm. (The origin of these is discussed below).

4.2 Results and Discussion

The ^{31}P nmr spectrum of $RuCl_2(CO)(PPh_3)_2$ dmf in $CDCl_3$ at 303K shows a singlet at 33.9 ppm which, on lowering the temperature to 213K shifts to 35.9 ppm. Since the far infra-red spectrum of the complex contains only a single terminal ruthenium chlorine stretch

(ν_{RuCl} 330s cm^{-1}) the complex probably has the structure (LX1), with trans- chlorides and trans- phosphines.



(LXI)

The ^{31}P nmr spectrum of $RuCl_2(CO)(PPh_3)_2$ MeOH (ν_{RuCl} 333 cm^{-1}) in $CDCl_3$ similarly shows a singlet at 34.5 ppm at 303K and 37.0 ppm at 213K.

When the latter complex was shaken in dichloromethane solution for 3 hours, the solvent partially removed and light petroleum (bp 60 - 80°C) added, the infra-red spectrum of the yellow complex obtained showed two carbonyl stretches (ν_{CO} 1970, 1930 cm^{-1}). The ^{31}P nmr spectrum at 213K showed a strong singlet at 36.9 ppm ($RuCl_2(CO)(PPh_3)_2MeOH$) and additional weaker signals at ca 54 and 40 ppm; a weak singlet at -7.3 (free PPh_3) is also present.

However, when $RuCl_2(CO)(PPh_3)_2MeOH$ is dissolved in CH_2Cl_2, light petroleum (bp 60 - 80°C) added and the solution warmed for ca 3 hours to permit the CH_2Cl_2 to evaporate, or ange crystals are deposited. The infra-red spectrum shows a broad band at 1960 cm^{-1} in the carbonyl region and bands at 312 cm^{-1} and 260 cm^{-1} in the regions for terminal and bridging chlorides.

The ^{31}P nmr spectrum at 213K in $CDCl_3$ showed a singlet at 37.0 (LXI; S = MeOH) superimposed on a complex series of resonances between 36 and 42 ppm; three other resonances were observed in the spectrum at 54.7, 53.6, and 53.2 ppm (fig. 20). On raising the temperature (293K) the complex pattern of resonances sharpened

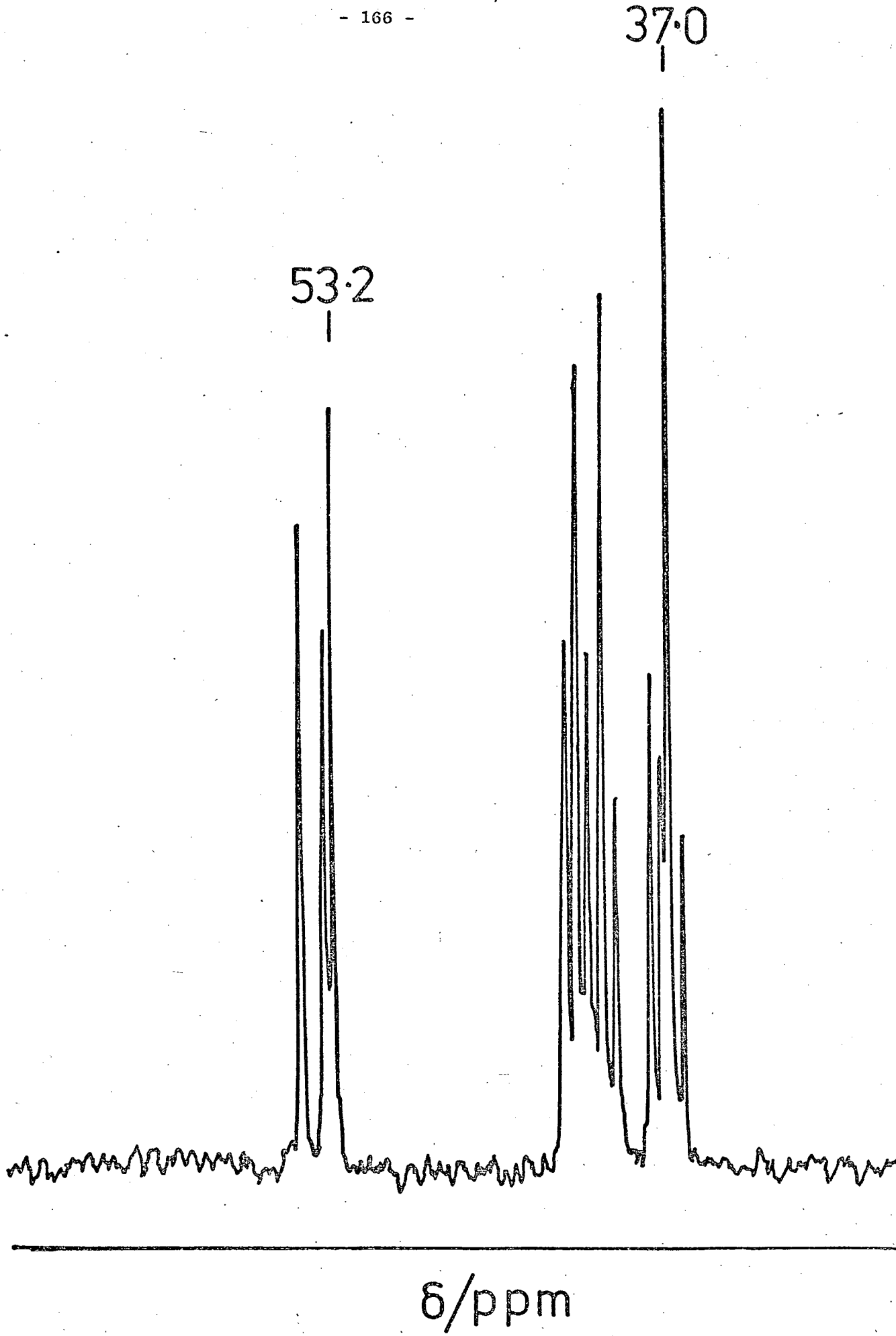


Figure 20 ^{31}P nmr spectrum in $CDCl_3$ at ca 213K of the product obtained on refluxing $RuCl_2CO(PPh_3)_2MeOH$ in CH_2Cl_2

shifting slightly to higher frequency whilst the singlet due to (LXI; S = MeOH) and the three resonances at ca 53 ppm move slightly to lower frequency.

This product whose spectrum is completely different to that described earlier for $[RuCl_2(CO)(PPh_3)_2]_2$ (except for the very weak resonances at ca 38, 42 and 52 ppm), may be obtained almost, but never completely, free from $RuCl_2CO(PPh_3)_2MeOH$ by repeated crystallisation (by the method described above) from CH_2Cl_2 and light petroleum (bp 60 - 80°C). It then analyses closely for the empirical formula $Ru_2Cl_4(CO)_2(PPh_3)_3$ (LXII). The latter is analogous to the corresponding yellow thiocarbonyl complex (LIII) formed from $[RuCl_2(CS)(PPh_3)_2]_2$ which shows ^{31}P nmr resonances in a similar position (see Chapter 3).

The ^{31}P nmr spectrum of (LXII) may be interpreted in terms of a mixture of the three isomeric forms (LXII a, b, c) (see Table 4:1). The phosphorus nucleus cis to CO and Cl in each isomer will give rise to a singlet and the two phosphorus nuclei cis to CO in each isomer will give an AB pattern of resonances. Thus the spectrum consists of three singlets 54.7, 53.6, 53.2 and three overlapping sets of AB quartets ca 36 to 42 ppm (see fig. 21). As it has not proved possible to separate the various isomeric forms by chromatography and as ^{31}P homonuclear decoupling was not possible, only a tentative assignment of the resonances to the various isomeric forms is possible.

It would be expected that since, in isomers (LXII b) and (LXII c) the unique phosphorus nucleus is eclipsed by another phosphorus atom that, in these two isomers the chemical shifts of these two nuclei would be very similar and hence the two singlets at 53.6 and 53.2 ppm may be assigned to the resonances of these two nuclei. This leaves the resonance of the unique phosphorus atom in isomer (LXII a)

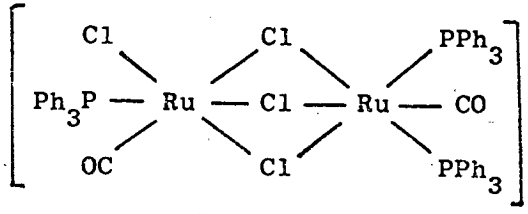
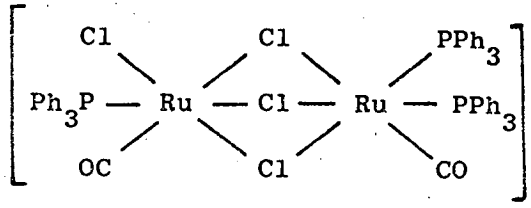
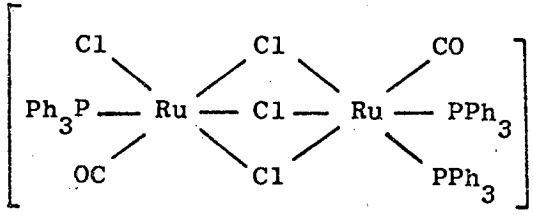
(eclipsed by CO) as the high frequency singlet at 54.7 ppm.

In the low frequency region of the spectrum three AB quartets may be distinguished, centred at 40.8 ppm (Jpp 25.4Hz; δ_{AB} 64.0Hz; ∇), 39.6 ppm (Jpp 25.3Hz; δ_{AB} 160.9; O) and 38.6 ppm (Jpp 25.5Hz; δ_{AB} 155.7Hz; X) respectively (see fig. 21).

Again, a tentative assignment of isomers to the AB resonances is possible, based on the values of δ_{AB}. Thus, two of the δ_{AB} values are very similar (ca 160Hz), suggesting these resonances arise from isomers in which one phosphorus atom is eclipsed by a phosphorus atom and the other by a carbonyl or a chloride group (isomers (LXII b) and (LXII c)). A further distinction cannot be made on this evidence. The other AB quartet has a much smaller δ_{AB} value (64.0Hz), indicating that the two phosphorus atoms are probably eclipsed by carbonyl and chloride groups respectively (isomer (XLII a) (see Table 4:1). It is interesting to note that all the ^{2}Jpp values (ca 25Hz) are consistent with cis- phosphines bound to ruthenium(II).

Support for this interpretation comes from the very recent synthesis of the analogous fluorophosphine complexes, $[(PPh_3)Cl(L)\text{-}RuCl_3Ru(L)(PPh_3)_2]$ (L = PF_3, Me_2NPF_2).[192] These complexes can be prepared by treatment of $RuH_2L(PPh_3)_3$ (L = PF_3) with gaseous HCl; reaction of $RuCl_2(PPh_3)_3$ with an equimolar amount of L (L = PF_3, Me_2NPF_2) in benzene solution; treatment of $[RuCl_2(PPh_3)_2$ acetone$]_2$ with PF_3; thermal decomposition of $RuCl_2L(PPh_3)_2$ dma (L = PF_3, Me_2NPF_2; dma = N, N' - dimethylacetamide; reaction between $RuCl_2(PPh_3)_3$ and cis-$RuCl_2(PF_3)_2(PPh_3)_2$ under reflux in acetone. A combination of ^{31}P and ^{19}F nmr spectroscopy provides unequivocal evidence for this formulation (LXII) and shows that, in this instance, an isomer of type (LXIIb) is the predominant one.

Table 4.1 Assignment of isomeric forms of $[(PPh_3)Cl(CO)RuCl_3Ru(CO)(PPh_3)_2]$ to ^{31}P nmr resonances

	Isomer (LXII)		^{31}P n.m.r. ($CDCl_3$ at 213K) Singlet Position (ppm)	AB Position (ppm)
(a)		∇	54.7	$40.8\ (\delta_{AB}\ 64.0\ Hz,\ J_{AB}\ 25.4\ Hz)$
(b)		O	53.6	$39.6\ (\delta_{AB}\ 160.9\ Hz,\ J_{AB}\ 25.5\ Hz)$
(c)		X	53.2	$38.6\ (\delta_{AB}\ 155.7\ Hz,\ J_{AB}\ 25.5\ Hz)$

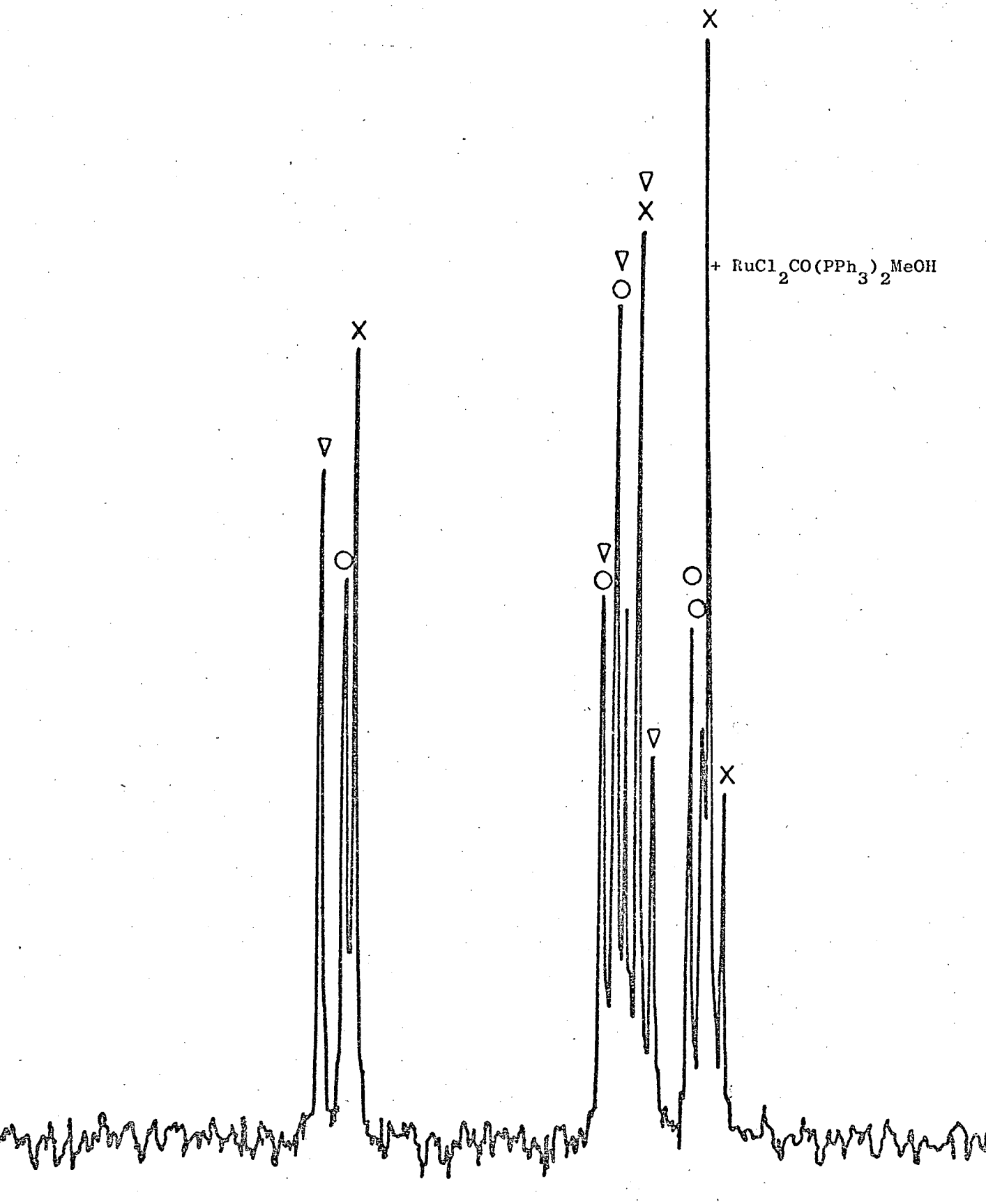


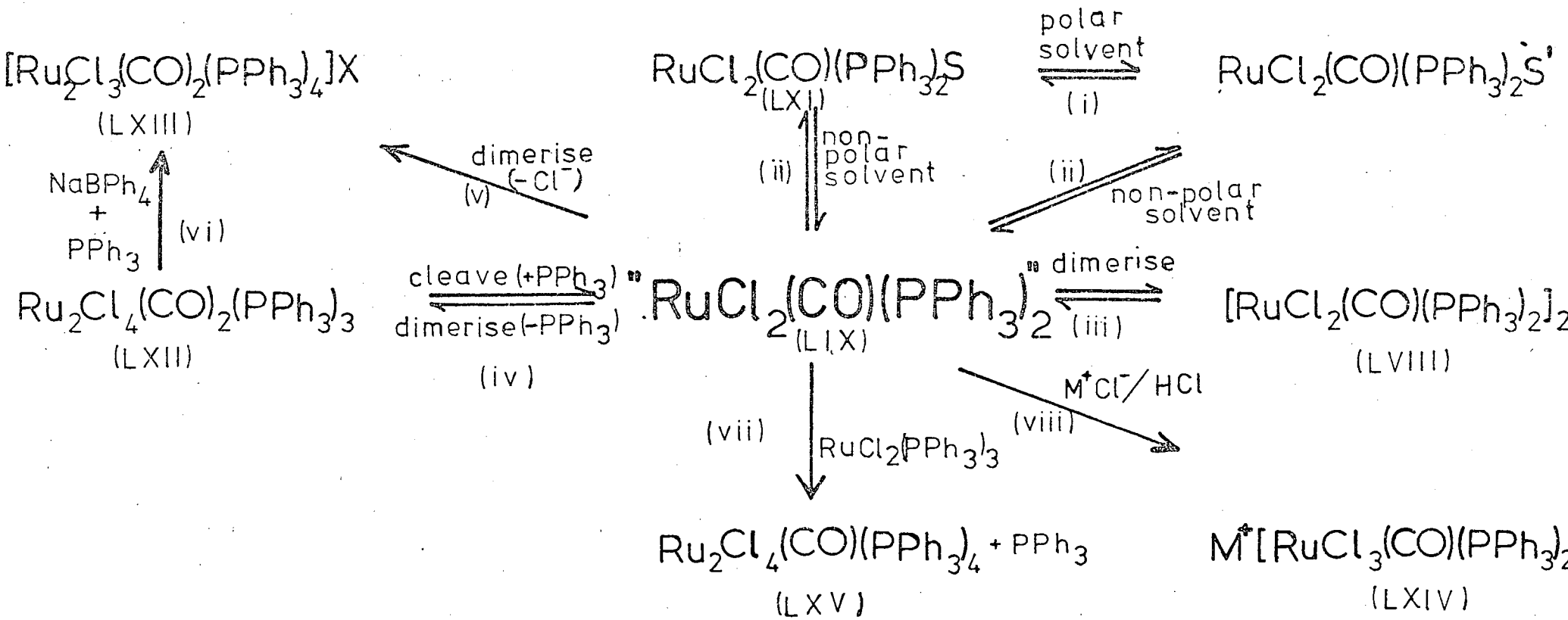
Figure 21 ^{31}P nmr spectrum in $CDCl_3$ at ca 213K of $Ru_2Cl_4(CO)_2(PPh_3)_3$ and $RuCl_2CO(PPh_3)_2MeOH$ showing assignment of resonances see pp 167, 168 and Table 4.1 p 169.

As the double halide bridged species is not observed in these reactions, this would support the proposed mechanism (Scheme 4:2) that the triple halide bridged species is formed by direct dimerisation of two monomers and not by intramolecular displacement of a ligand from a double halide bridged intermediate.

Recently the complex $Ru_2Cl_4(CO)_2(PPh_3)_3$ has been prepared by treatment of the complexes $RuHClCO(PPh_3)_3$ and $RuH_2CO(PPh_3)_3$ with gaseous HCl.[193,192] These reactions probably proceed via a similar reaction pathway; the first step involving the formation of $RuCl_2(CO)(PPh_3)_3$ which then forms the five coordinate intermediate "$RuCl_2(CO)(PPh_3)_2$" (LIX) (by loss of PPh_3) and this will then react as discussed previously (see Schemes 4:1 and 4:2). In the reaction with $RuHCl(CO)(PPh_3)_3$, trans $RuCl_2(CO)_2(PPh_3)_2$ is also formed,[193] presumably by decarbonylation of the solvent (ethanol). ^{31}P nmr spectroscopy has shown that the same isomer mixture of $Ru_2Cl_4(CO)_2(PPh_3)_3$ is formed whether the complex is prepared from $RuCl_2(CO)(PPh_3)_2S$ (S = MeOH or dmf) or from $RuHCl(CO)(PPh_3)_3$.[188]

As the double halide bridged complex (LVIII) could not be isolated when $RuCl_2(CO)(PPh_3)_2MeOH$ was reacted in dichloromethane solution, other solvents were used. In less polar solvents such as benzene the triple halide bridged complex (LXII) was again obtained. However, when the reaction was performed in a more polar solvent such as acetone, the pale yellow complex obtained showed two carbonyl absorption bands (ν_{CO} 1978 br, 1928 cm^{-1}) in the infra-red spectrum.

The ^{31}P nmr spectrum of the complex in $CDCl_3$ solution at 243K showed a singlet at 37.0 ppm ($RuCl_2(CO)(PPh_3)_2MeOH$). In addition the three singlets of the isomers of (LXII) are observed as weak resonances at ca 54 ppm as are the AB patterns which appear at ca 41 ppm. However, superimposed upon these latter signals is another more intense AB pattern

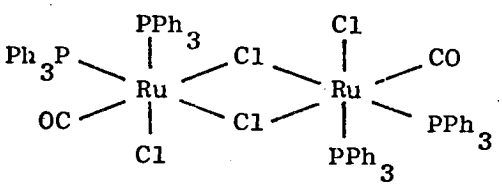

[Ru2Cl3(CO)2(PPh3)4]X
(LXIII)
NaBPh4 + PPh3
(vi)
Ru2Cl4(CO)2(PPh3)3
(LXII)
dimerise (-Cl⁻)
(v)
RuCl2(CO)(PPh3)2S
(LXI)
(ii) non-polar solvent
polar solvent
(i)
RuCl2(CO)(PPh3)2S'
(ii) non-polar solvent
cleave (+PPh3)
dimerise (-PPh3)
(iv)
RuCl2(CO)(PPh3)2
(LIX)
dimerise
(iii)
[RuCl2(CO)(PPh3)2]2
(LVIII)
(vii) RuCl2(PPh3)3
M⁺Cl⁻/HCl
(viii)
Ru2Cl4(CO)(PPh3)4 + PPh3
(LXV)
M⁺[RuCl3(CO)(PPh3)2]⁻
(LXIV)

Scheme 4·2

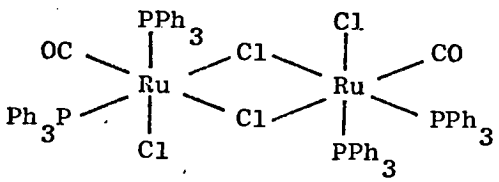
(see fig. 22) centred at 40.6 ppm with a different set of parameters (Jpp 25.6 Hz; δ_{AB} 115 Hz) from those observed for $Ru_2Cl_4(CO)_2(PPh_3)_3$ (LXII); other weak broad resonances are observed at ca 26 and 18 ppm (cf.$[RuCl_2(CO)(PPh_3)_2]_2$)[191] and there is a singlet at -7 ppm (free PPh_3).

When $RuCl_2(CO)(PPh_3)_2MeOH$ is shaken in ethanol (in the presence of an excess of triphenylphosphine) the infra-red again shows two carbonyl bands (ν_{CO} 1978 br and 1928 cm^{-1}). The ^{31}P nmr of the complex in $CDCl_3$ solution at 213K shows only weak signals corresponding to $Ru_2Cl_4(CO)_2(PPh_3)_3$, the spectrum comprising mainly the AB pattern of resonances (centred at 40.6ppm) and two singlets 37.0 (LXI; S = MeOH) and 35.9 ppm (LXI; S = EtOH). Other weak broad resonances are observed at ca 26, 17.6, 12.5, 6.0 and -0.1 ppm. The weak resonances below 26 ppm may be attributed to the presence of $[RuCl_2(CO)(PPh_3)_2]_2$. (The peaks at 26, 17.6 were observed previously;[191] the others are assigned to different isomeric forms of (LVIII)).

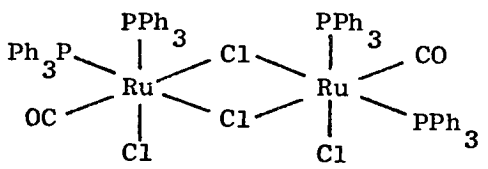
The AB set centred at 40.6 ppm could arise from an isomer of $[RuCl_2(CO)(PPh_3)_2]_2$ such as (LVIII a-d) in which one of the phosphine



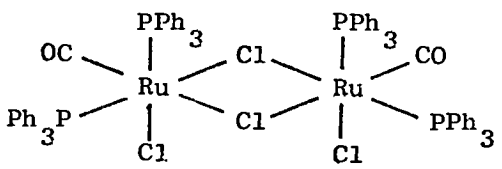
(LVIII a)



(LVIII b)



(LVIII c)



(LVIII d)

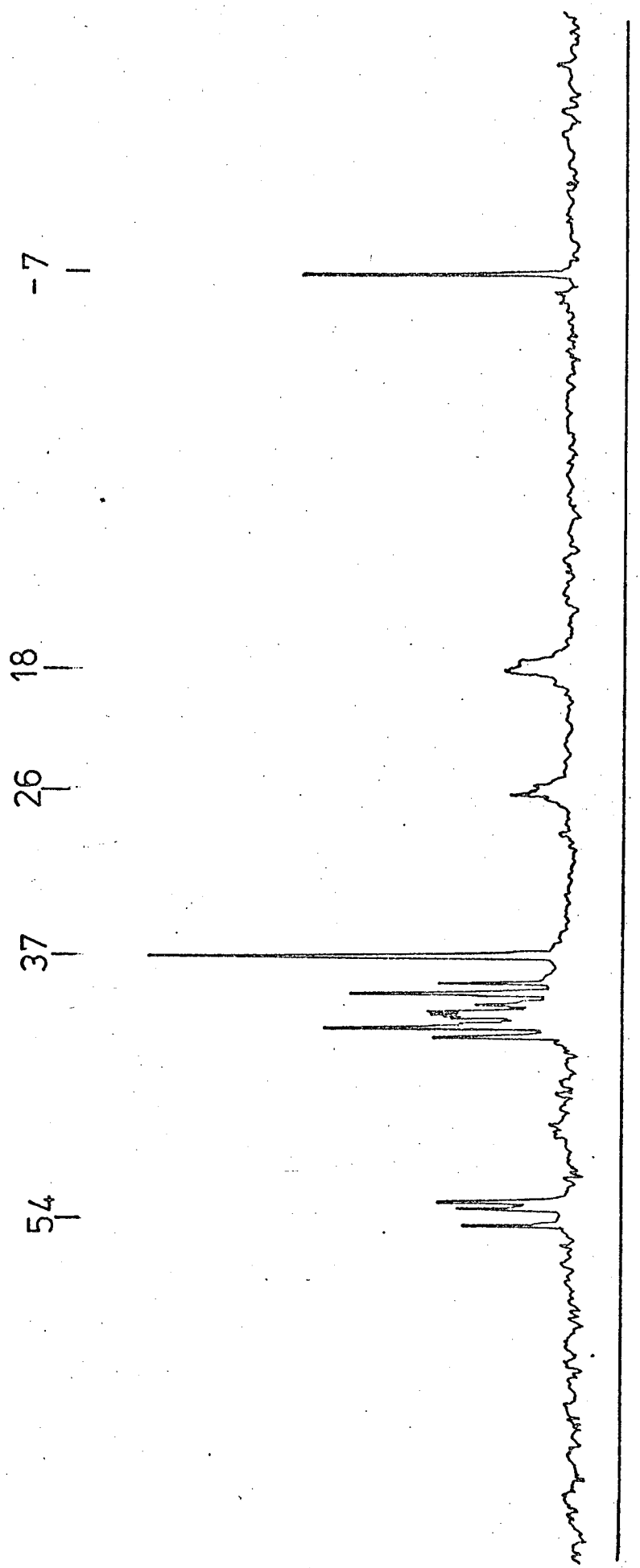
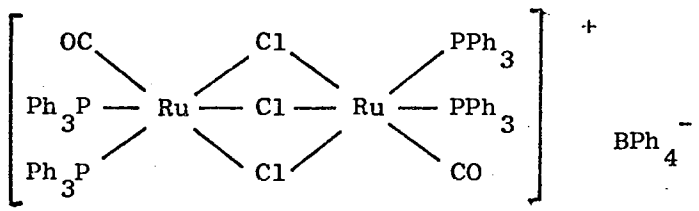


Figure 22. ^{31}P nmr spectrum in $CDCl_3$ at ca 243K of the product obtained on refluxing $RuCl_2CO(PPh_3)_2$ MeOH in acetone.

ligands is trans- to a bridging chloride group and the other trans- to a terminal chloride group. However if these resonances did correspond to such a complex, it would be reasonable to expect that these resonances might be observed in the spectra of the products from the reactions performed in other solvents. (Although non-polar solvents such as benzene might be expected to favour trans- configurations (low dipole moment), some of the cis- complexes should form in the more polar dichloromethane.)

However, when $Ru_2Cl_4(CO)_2(PPh_3)_3$, triphenylphosphine and sodium tetraphenylborate are shaken together in dichloromethane, acetone or ethanol solution, a pale yellow complex is obtained whose infra-red spectrum shows a broad carbonyl absorption band at 1978 cm^{-1}. Solutions of the complex in dichloromethane are conducting ($\Lambda_{10^{-3}M} = 30\Omega^{-1}\ cm^2\ mol^{-1}$). The ^{31}P nmr spectrum (in $CDCl_3$ at 213K) of this complex which analyses closely for $[Ru_2Cl_3(CO)_2(PPh_3)_4]BPh_4$ shows an AB quartet (centred at 40.8 ppm; Jpp 27.1 Hz; δ_{AB} 113.3 Hz)(see fig. 23) consistent with the structure (LXIII) and identical to that observed in the spectra of the products from the acetone and ethanolic reactions of $RuCl_2CO(PPh_3)_2MeOH$. Solutions of the latter in acetone are slightly conducting indicating the presence of a small amount of the ionic complex $[Ru_2Cl_3(CO)_2(PPh_3)_4]Cl$.



(LXIII)

In terms of the scheme (4:2) this complex could be formed either directly from $Ru_2Cl_4(CO)_2(PPh_3)_3$ by intermolecular displacement of chloride by triphenylphosphine (step (vi)) or by dimerisation of

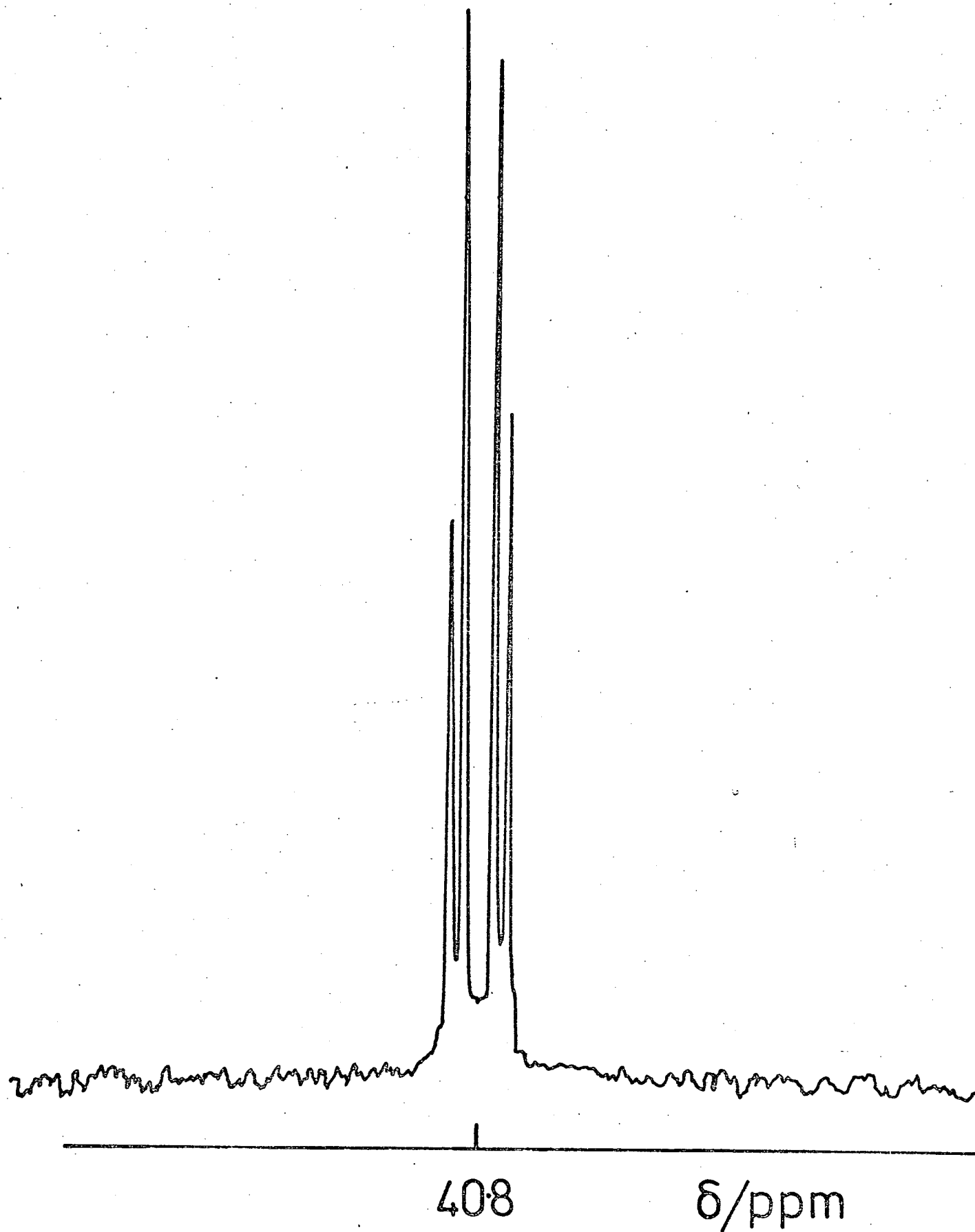
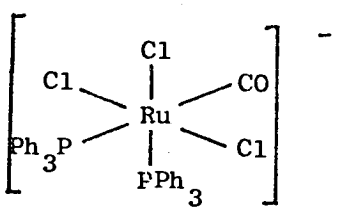


Figure 23 ^{31}P nmr spectrum in $CDCl_3$ at ca 213K of $[Ru_2Cl_3(CO)_2(PPh_3)_4]BPh_4$

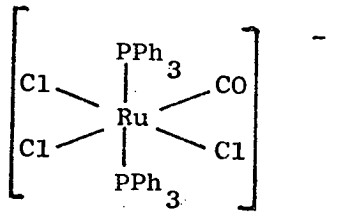
"$RuCl_2CO(PPh_3)_2$" accompanied by loss of a chloride group (step (v)).

The double halide bridge of the complex $[RuCl_2(CS)(PPh_3)_2]_2$ (LI) has been shown to undergo cleavage with chloride ion giving the anionic $[RuCl_3(CS)(PPh_3)_2]^-$ (LVI). Although the corresponding carbonyl complex (LVIII) can not be isolated in a pure form, the reaction with chloride ion in the presence of a large cation to produce the anion $[RuCl_3(CO)(PPh_3)_2]^-$ (LXIV) may be performed <u>in situ</u> by reaction of $RuCl_2(CO)(PPh_3)_2S$ (S = dmf or MeOH) with $Ph_4AsCl.HCl$ and HCl in acetone in the presence of excess PPh_3. When the reaction is performed in small amounts of solvent over a short reaction time, yellow crystals of the complex $Ph_4As[RuCl_3(CO)(PPh_3)_2]$ acetone [ν_{CO} 1918 cm^{-1}: $\Lambda_{10^{-3}M} = 45\Omega^{-1}\ cm^2\ mol^{-1}$ (CH_2Cl_2)] are isolated.

The complex has a very strong band in the far infra-red at 320cm^{-1}, characteristic of a <u>trans-</u> $RuCl_2$ arrangement[129] and consistent with structures (LXIV a or LXIV b).



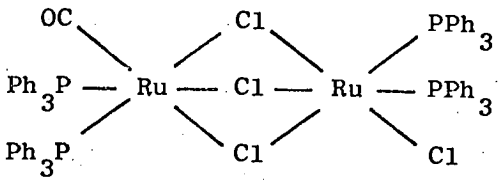
(LXIV a)



(LXIV b)

Like the corresponding $M[RuCl_3(CS)(PPh_3)_2]$ (M = Ph_4As^+, $Ph_3(PhCH_2)P^+$, Et_4N^+),[179] (LXIV) is too poorly soluble for satisfactory ^{31}P nmr studies.

When $RuCl_2CO(PPh_3)_2$dmf is refluxed with $RuCl_2(PPh_3)_3$ in acetone (1:1 molar ratio), red crystals of the tri-μ-halo- complex $Ru_2Cl_4CO(PPh_3)_4$ acetone (ν_{CO} 1951 cm^{-1}; ν_{RuCl} 319s, 250br cm^{-1})(LXV) are formed in high yield.



(LXV)

X-ray diffraction studies[194] on this complex show that it is isomorphous with the corresponding thiocarbonyl complex (LII).[181] The ^{31}P nmr spectrum in $CDCl_3$ at 213K consists of two AB quartets (fig. 24) (cf. spectrum of $Ru_2Cl_4(CS)(PPh_3)_4$, fig. 19) centred at 48.0 ppm (Jpp 37.5 Hz; δ_{AB} 97.7 Hz) and 40.3 ppm (Jpp 24.6 Hz; δ_{AB} 74.2 Hz). This spectrum confirms the assignment of the high frequency resonance to the phosphorus nuclei cis- to the chloride group, as the difference in position between the two high frequency quartets in the CO and CS complexes is only 0.3 ppm compared with the other, much larger change of 4.2 ppm in the position of the low frequency quartets on going from carbonyl to thiocarbonyl. The low frequency shift on changing from CS to CO indicates the greater shielding effect of the latter.

This reaction confirms the hypothesis that the triple halide bridged compounds $Ru_2Cl_4(Y)(PPh_3)_4$ (Y = CS,CO) are formed by dimerisation of two monomers (scheme 3:1 step (v) and scheme 4:2 step (vii)) and not via the double halide intermediate $[RuCl_2(Y)(PPh_3)_2]_2$. A related reaction is the formation of $(PPh_3)_2ClRuCl_3Ru(PF_3)(PPh_3)_2$ from $RuCl_2(PPh_3)_3$ and PF_3 (2:1 molar ratios)[192] which, presumably involves initial formation of an intermediate such as "$RuCl_2(PF_3)(PPh_3)_2$" followed by coupling with unreacted $RuCl_2(PPh_3)_3$. Similarly, coupling of species such as "$RuCl_2(N_2)(PPh_3)_2$" and $RuCl_2(PPh_3)_3$ could be invoked to explain the formation of $(PPh_3)_2ClRuCl_3Ru(N_2)(PPh_3)_2$ from $RuCl_2(PPh_3)_4$ and

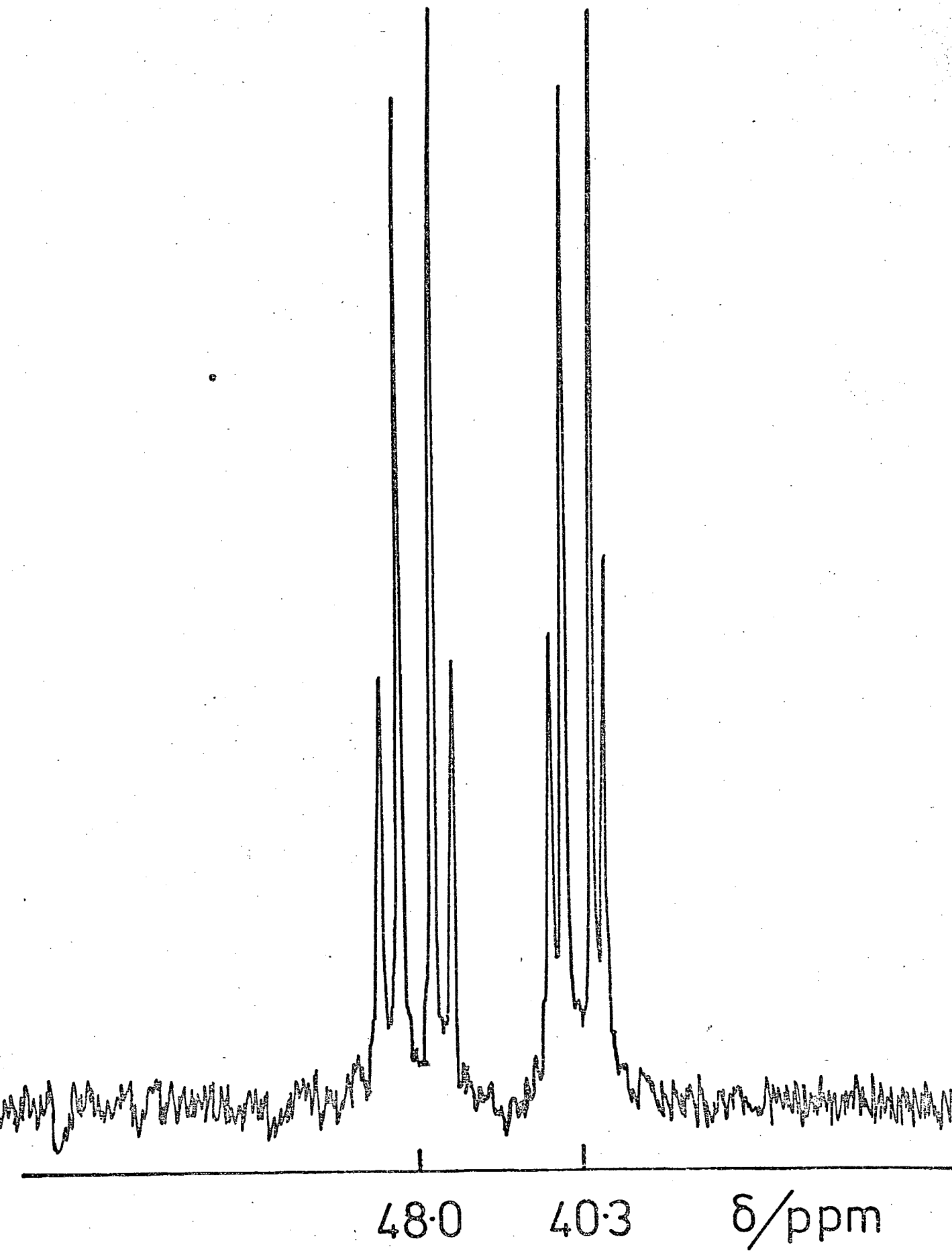


Figure 24 ^{31}P nmr spectrum of $Ru_2Cl_4CO(PPh_3)_4$ in $CDCl_3$ at ca 213K.

molecular nitrogen in a reverse osmosis cell.[184]

When $Ru_2Cl_4(CS)(PPh_3)_4$ is treated with HCl in an acetone suspension the mixed ruthenium(II) ruthenium(III) species (LVII) is obtained. However $Ru_2Cl_4(CO)(PPh_3)_4$ is stable to oxidation by HCl being recovered unreacted after shaking in an acetone/hydrochloric acid suspension for 3 months.

The "coupling reaction" between $RuCl_2(PPh_3)_3$ and $RuCl_2CO(PPh_3)_2S$ (S = dmf, MeOH) used to prepare the triple halide bridged complex (LXV) was extended in an attempt to synthesise complexes containing mixed halide bridges and mixed tertiary phosphine complexes.

Thus, when $RuCl_2CO(PPh_3)_2$dmf is refluxed in acetone with an equimolar amount of $RuBr_2(PPh_3)_3$, a deep red crystalline complex (ν_{CO} 1952 cm^{-1}) which analyses well (C,H,Cl,Br) for the empirical formula $Ru_2Cl_2Br_2(CO)(PPh_3)_4$ acetone can be isolated in high yield.

A similar red compound (ν_{CO} 1953 cm^{-1}) with the same empirical formula is obtained by the corresponding reaction between $RuBr_2CO(PPh_3)_2$dmf and $RuCl_2(PPh_3)_3$. The far infra-red spectra of the two complexes are very similar, the latter having a stronger band at 317 cm^{-1}(νRu-Cl).

However, the ^{31}P nmr spectra of both samples in $CDCl_3$ solution appear identical both in the presence and absence of air, comprising two complex series of resonances (ca 52 to 46 ppm and ca 42 to 35 ppm) (see fig. 25).

Complete analysis of these spectra has, to date, proved impossible but a close examination of both the low and high frequency sets of resonances indicate that they consist of a series of overlapping AB quartets. Although it is reasonable to expect that each of the coupling reactions will generate the two different sets of three

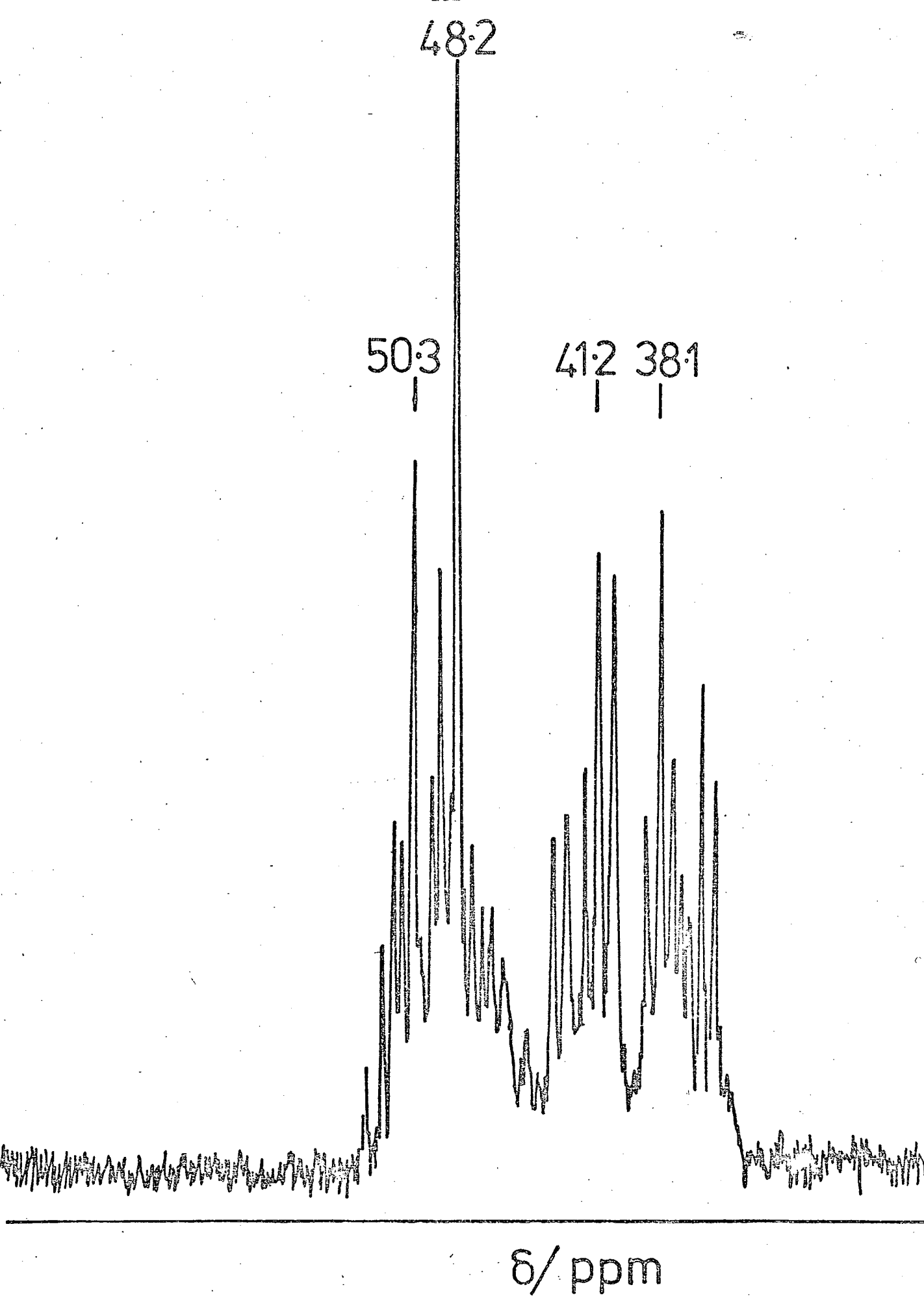
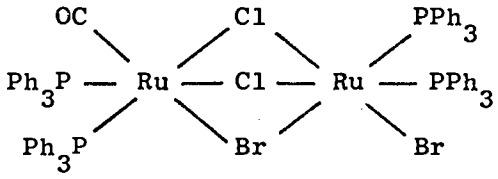
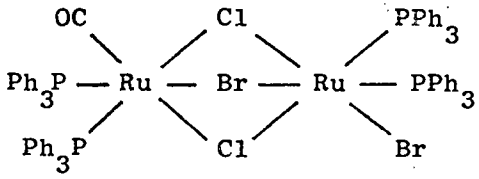


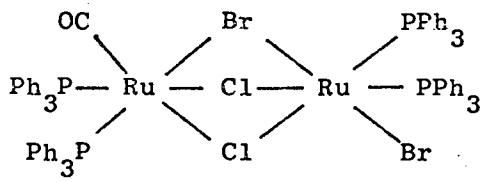
Figure 25 ^{31}P nmr spectrum of $Ru_2Cl_2Br_2CO(PPh_3)_4$ in $CDCl_3$ at ca 210K.

Figure 26 Geometrical isomers of $RuCl_2Br_2CO(PPh_3)_4$†

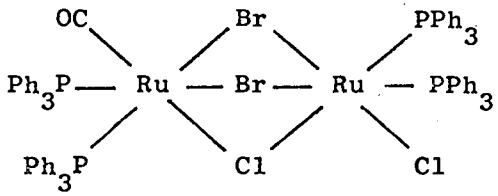
a) with two bridging Cl groups

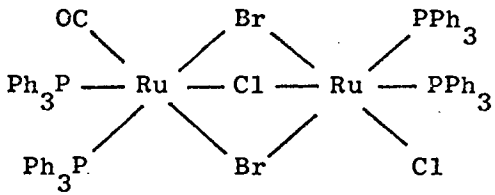


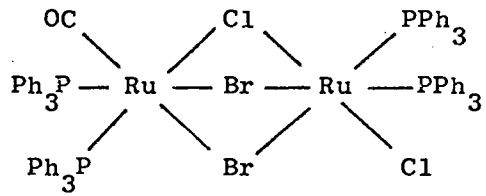




b) with two bridging Br groups

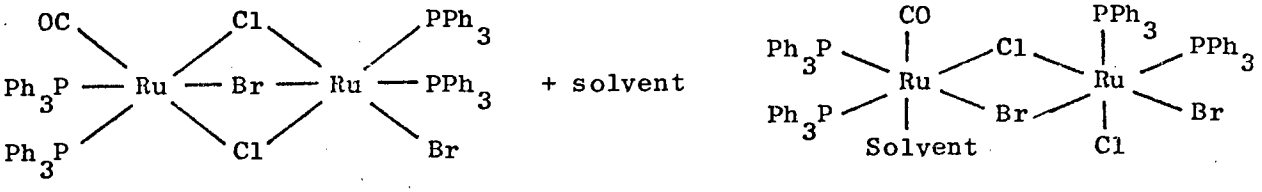


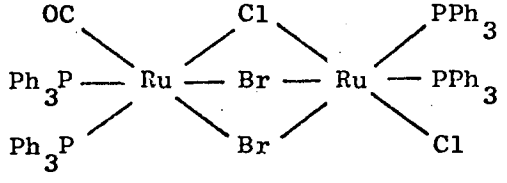




† assumes arrangement of terminal ligands is as in $Ru_2Cl_4CO(PPh_3)_4$

geometrical isomers (shown in figures 26a and 26b respectively)†, each of which will produce slightly different ^{31}P nmr AB quartets, the identical nature of the spectra given by both products in solution is at first sight rather puzzling. The best explanation of this is the occurrence of facile, solvent-assisted, partial, bridge opening reactions in solution, which leads to scrambling of terminal and bridging ruthenium chloride and bromide bonds, with consequent formation of some of all six possible isomers in each solution (e.g. equation 23).





+ solvent. . . . (23)

An X-ray structural analysis of the product from reaction of $RuBr_2(PPh_3)_3$ and $RuCl_2(CO)(PPh_3)_2dmf$ is in progress, in an attempt to ascertain if the complex initially consists of a mixture of all three isomeric forms or whether they are formed on dissolution.

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†Note that only these six geometrical isomers are possible if the four PPh_3 groups are arranged as in $[(PPh_3)_2ClRuCl_3Ru(Y)(PPh_3)_2]$ (Y = CS, CO).

Hoffman and Caulton[70] report that the literature preparation of $RuBr_2(PPh_3)_3$[114] gives a mixture of three species, $RuBr_2(PPh_3)_3$, $RuBrCl(PPh_3)_3$ and $RuCl_2(PPh)_3$ in a mole ratio of 4.9: 4.7: 1, and this in fact might explain the formation of a mixture containing all six isomers. However, $RuBr_2CO(PPh_3)_2$dmf analyses correctly in C,H,Br for this formulation (see ref 190) as does $RuBr_2(PPh_3)_3$ (see ref 114)† and furthermore, the ^{31}P nmr spectra indicate that there is no $Ru_2Cl_4(CO)(PPh_3)_4$ present in the products, suggesting no contamination of $RuBr_2(PPh_3)_3$ by $RuCl_2(PPh_3)_3$.

When $RuBr_2(CO)(PPh_3)_2$dmf and $RuBr_2(PPh_3)_3$ are refluxed together in acetone a black complex (ν_{CO} 1952 cm^{-1}) is obtained which analyses well (C,H,Br) for the complex $Ru_2Br_4(CO)(PPh_3)_4$. This compound is very poorly soluble in the absence of air in the common organic solvents. The ^{31}P nmr spectrum in $CDCl_3$ (of sample exposed to the air) shows two complex series of resonances (51 to 46 ppm and 42 to 34 ppm) (different to that observed for the mixed Br/Cl complexes described above) and also a singlet at 31 ppm ($OPPh_3$). It may be in this case that in the presence of air, bridge opening is occurring.

If $RuCl_2CO(PPh_3)_2$dmf and $RuCl_2(PEtPh_2)_3$ are refluxed together in acetone (1:1 molar ratios) for 3 hours and the solvent removed from the resulting orange-red solution, a bright orange product is obtained (ν_{CO} 1960). However, the ^{31}P nmr spectrum could not be

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† Other analytical evidence for various products of reactions using $RuBr_2(PPh_3)_{3 \text{ or } 4}$ as a starting material (see chapter 2 and references 132, 158, 174, 179, 195, 196) support the formulation as in reference (114).

resolved, containing 63 resonance lines. The complexity of the spectrum is probably due to the fact that free ethyldiphenyl phosphine is generated during the reaction and this will then further react either with unreacted $RuCl_2(PPh_3)_3$ or with the product $(PPh_3)_2CORuCl_3RuCl(PEtPh_2)_2$ displacing triphenylphosphine. In addition (as discussed in chapter 2) the complex $RuCl_2(PEtPh_2)_3$ may also dimerise to the corresponding triple bridged complex $Ru_2Cl_4(PEtPh_2)_5$. Because of these complexities, further reactions of this type were not pursued.

4.3 Conclusions

The mechanism outlined in scheme 3:1 is substantiated by the reactions of the corresponding carbonyl compounds. Although the double halide bridged dimer (LVIII) may not be isolated in a pure state, (unlike the corresponding thiocarbonyl complex (LI)), it may be observed in the ^{31}P nmr spectrum as a transient species in solutions of $RuCl_2(CO)(PPh_3)_2S$ (S = dmf, MeOH). $[RuCl_2(CO)(PPh_3)_2]_2$ would therefore appear to be less stable in solution than the corresponding thiocarbonyl complex.

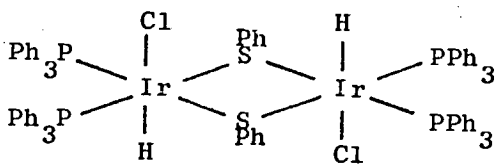
Mechanisms similar to those outlined in schemes 3:1 and 4:2 can be invoked to explain the rearrangement reactions of other complexes. (The rearrangements of $[RhCl_2(C_5Me_5)]_2$, $[RuCl_2(arene)_2]_2$ and $[IrHCl(SPh)(PPh_3)_2]_2$ have already been discussed in chapter 3).

For example, Barnard *et al*[197] have observed that the compound $[RuCl_2(CO)(PMe_2Ph)_2]_2$ (LXVI) (ν_{CO} 1978 cm^{-1}) is deposited slowly from the mother liquor remaining from the irradiative conversion of *cis*-$Ru(CO)_2(PMe_2Ph)_2Cl_2$ into the corresponding all-*trans*-isomer. The formation of (LXVI) is explained in terms of the dimerisation of a

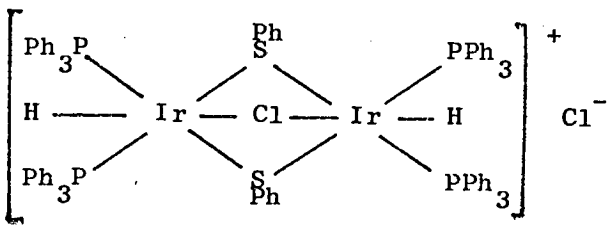
five coordinate intermediate $RuCl_2(CO)(PMe_2Ph)_2$ (LXVII) analogous to the formation of $[RuCl_2(CO)(PPh_3)_2]_2$ from "$RuCl_2(CO)(PPh_3)_2$" (LIX) (scheme 4:2 step (iii)).

Another closely related double chloride bridged complex whose formation can be described in terms of the scheme is $[RuCl_2(CO)_2(PPh_3)]_2$ (ν_{CO} 2076s, 2016s cm^{-1})[198] which is formed from the mononuclear $RuCl_2(CO)_3(PPh_3)$ (ν_{CO} 2133m, 2075s, 2033m cm^{-1}). The formation of $[RuCl_2(CO)_2(PPh_3)]_2$ probably occurs by dissociation of a carbonyl group from the six coordinate monomer to form the five coordinate intermediate "$RuCl_2(CO)_2PPh_3$" which then dimerises.

Senoff et al[185,199] have shown that when $IrCl(PPh_3)_3$ is reacted with HSPh the dimeric Iridium (III) complex $[(PPh_3)_2HCl\text{-}IrSPh]_2$ (LXVIII) is obtained and that when (LXVIII) is dissolved in $CHCl_3$ the triple bridged dimer $[Ir_2H_2Cl(SPh)_2(PPh_3)_4]Cl$ (LXIX) can be precipitated by the addition of petroleum ether (bp 63-75°C).

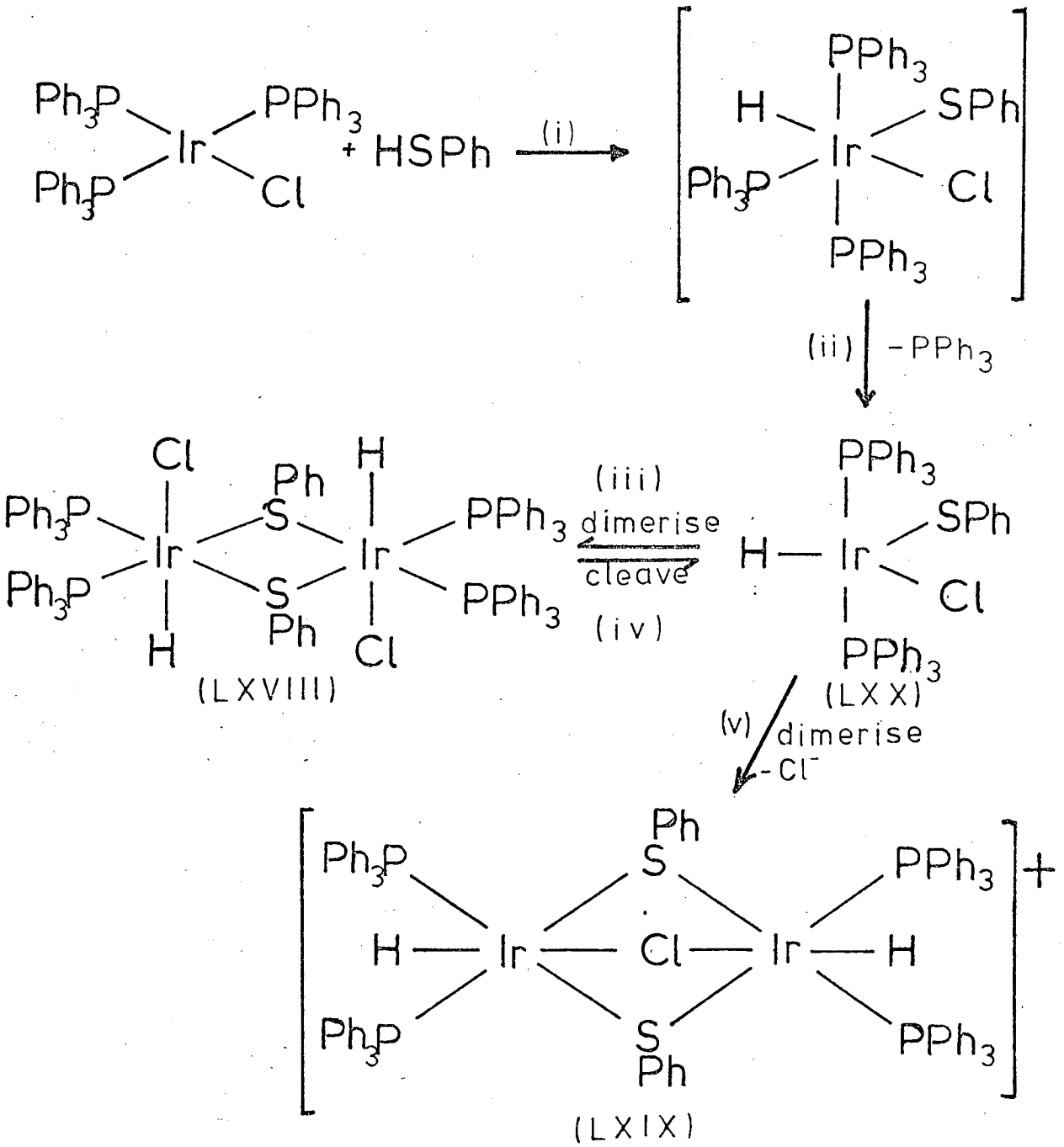


(LXVIII)



(LXIX)

The formation of (LXVIII) is interpreted in terms of the formation and dimerisation of a five coordinate intermediate "$IrHClSPh(PPh_3)_2$" (LXX)(see scheme 4:3). By analogy with the ruthenium systems outlined in schemes 2:1, 3:1 and 4:2 it would seem probable that the triple bridged species is formed from the double bridged species via cleavage (step (iv)) to form (LXX) followed by dimerisation accompanied by loss of Cl^- (step (v)).



Reaction of $IrCl(PPh_3)_3$ with SPh: mechanism taken in part from refs. 185,199

Scheme 43

4.4 Experimental

Physical measurements were as described in chapter 2. All infra-red spectra quoted in this chapter (4000-250 cm^{-1}) were measured using nujol mulls on caesium iodide plates.

Carbonyldichloro(methanol)bis(triphenylphosphine)ruthenium(II):-

$[RuCl_2(CO)(PPh_3)_2dmf]$ (190) (^{31}P nmr ($CDCl_3$ at 303K) 33.9 ppm (singlet); ν_{RuCl} 331 cm^{-1}) was recrystallised from hot methylene-chloride/methanol to give the yellow product which was washed with diethyl ether (Found: C, 60.3; H, 4.3; Cl, 9.1. Calc for $C_{38}H_{34}Cl_2O_2P_2Ru$: C, 60.5; H, 4.5; Cl, 9.4%) ^{31}P nmr ($CDCl_3$) 34.5 ppm (singlet), (ν_{CO} 1931, 1921 cm^{-1} [nujol]; 1940 cm^{-1} CH_2Cl_2); ν_{RuCl} 333 cm^{-1}. At 213K, singlets in ^{31}P nmr spectrum are found at 35.9 and 37.0 ppm for dmf and MeOH solvents respectively.

Reaction of $RuCl_2(CO)(PPh_3)_2MeOH$ in dichloromethane:-

$RuCl_2(CO)(PPh_3)_2MeOH$, was shaken in CH_2Cl_2 for three hours under nitrogen. Most of the solvent was removed from the resulting yellow solution and light petroleum (bp 60-80°C) was added. The mixture was evaporated to a small volume and the resulting yellow solid filtered and washed with diethyl ether.

For discussion of i.r. and ^{31}P nmr of this product see page 165.

Tri-μ-chloro[carbonylchloro(triphenylphosphine)ruthenium(II)][carbonylbis-(triphenylphosphine)ruthenium(II)]:-

$[RuCl_2(CO)(PPh_3)_2MeOH]$ was dissolved in dichloromethane and light petroleum (bp 60-80°C) was added. The yellow solution was warmed gently on a waterbath for several hours to allow the dichloro-methane to evaporate slowly. The resulting orange solid was re-dissolved in dichloromethane, light petroleum (bp 60-80°C) added and the process repeated to give pale orange crystals of the product which

were filtered and washed with ethanol and diethylether m.p. 247°C (ν_{CO} 1960 cm^{-1} (broad) [nujol]) (Found: C, 58.7; H, 4.1. Calc. for $C_{56}H_{45}Cl_4O_2P_3Ru_2$: C, 56.7; H, 3.8%) ^{31}P nmr ($CDCl_3$ at 213K) (Figure 21) see page 166. The slightly high carbon and hydrogen figures are due to the presence of some unreacted [$RuCl_2(CO)(PPh_3)_2MeOH$] (see Figure 21).

Tri-μ-chloro-bis[carbonylbid(triphenylphosphine)ruthenium(II)] tetraphenylborate:-

The [$(PPh_3)Cl(CO)RuCl_3Ru(CO)(PPh_3)_2$] isomer mixture (0.12 g), $NaBPh_4$ (0.034 g) and PPh_3 (0.026 g) were shaken together in degassed dichloromethane (25 cm^3) under nitrogen for 50 h. The solution was evaporated to dryness, triturated with methanol and the resulting solid filtered off and washed with water, methanol and diethylether (0.14 g, 80%) m.p. 124-126°C (ν_{CO} 1976 cm^{-1} [nujol]) (Found: C, 66.7; H, 4.9. Calc. for $C_{98}H_{80}BCl_3O_2P_4Ru_2$: C, 67.9; H, 4.6%) ^{31}P nmr in $CDCl_3$ at 213K, 40.8 (quartet) ppm Jp_Ap_B 27.1; δp_Ap_B 113.3Hz [Λ(1 x 10^{-3} M) in CH_2Cl_2 = 30 Ω^{-1} cm^2 mol^{-1}].

[$Ru_2Cl_3(CO)_2(PPh_3)_4$]Cl was also formed by shaking [$RuCl_2CO(PPh_3)_2MeOH$] in either acetone or ethanol for 3 h (^{31}P nmr evidence) with or without free PPh_3 present. In these reactions, the [$Ru_2Cl_4(CO)_2(PPh_3)_3$] isomer mixture and traces of [$RuCl_2CO(PPh_3)_2$]$_2$ were also found.

Tetraphenylarsoniumcarbonyl(trichloro)bis(triphenylphosphine)ruthenate(II)acetone (1:1):-

[$RuCl_2(CO)(PPh_3)_2MeOH$] (0.10 g) was suspended in degassed acetone (30 cm^3) and treated with a two-fold excess of $Ph_4AsCl.HCl$ together with triphenylphosphine (ca 0.01 g). The mixture was shaken for 4 h when orange yellow crystals of the product precipitated.

These were filtered off, washed with water, methanol and diethylether and dried in *vacuo* at 40°C (0.13 g; 70%) m.p. 155-158°C (ν_{CO}(acetone) 1710 cm^{-1} [nujol]) (Found: C, 64.1; H, 4.7; Cl, 9.0. Calc. for $C_{64}H_{56}AsCl_3O_2P_2Ru$: C, 64.0; H, 4.7; Cl, 8.9%) [Λ(1 x 10^{-3} M) in CH_2Cl_2 = 45 Ω^{-1} cm^2 mol^{-1}].

Tri-μ-chloro-[chlorobis(triphenylphosphine)ruthenium(II)][carbonylbis(triphenylphosphine)ruthenium(II)]-acetone (1/2):-

The complexes [$RuCl_2(PPh_3)_3$] (0.12 g) and [$RuCl_2(CO)(PPh_3)_2$dmf] (0.10 g) were heated together under reflux for 2.5 h in degassed acetone (30 cm^3) under an atmosphere of nitrogen. The solution was then cooled and the deep red crystals of product were filtered off and washed with diethylether. Further crystals of the complex were obtained by evaporation of the filtrate to *ca* 10 cm^3 (0.13 g; 69%) m.p. 170-171°C (decomp) (ν_{CO} 1951 cm^{-1}, ν_{CO} (acetone) 1710 cm^{-1} [nujol]) (Found: C, 61.7; H, 4.7; Cl, 9.4 Calc. for $C_{79}H_{72}Cl_4O_3P_4Ru_2$: C, 61.6; H, 4.8; Cl, 9.3%) *^{31}P nmr* ($CDCl_3$ at 298K) (Figure 24) 48.0 (quartet); 40.3 (quartet) ppm (Jp_1p_2 37.5, Jp_3p_4 24.6; δp_1p_2 97.7, δp_3p_4 74.2 Hz).

Reaction of $Ru_2Cl_4(CO)(PPh_3)_4$ with HCl:-

$Ru_2Cl_4(CO)(PPh_3)_4$ was suspended in acetone and concentrated hydrochloric acid and excess $Ph_4AsCl.HCl$ were added. The mixture was shaken for three months. Most of the solvent was then removed from the resulting dark solution from which $Ru_2Cl_4CO(PPh_3)_4$ precipitated.

μ-Bromo-di-μ-chloro-[bromobis(triphenylphosphine)ruthenium(II)][carbonylbis(triphenylphosphine)ruthenium(II)]-acetone (1/1):-

[$RuBr_2(PPh_3)_3$] (0.12 g) and [$RuCl_2CO(PPh_3)_2$dmf] (0.08 g) were heated together under reflux for 3 h in degassed acetone (30 cm^3) under an atmosphere of nitrogen. The solution was then cooled and

the deep red precipitate filtered and washed with diethylether (0.10 g; 56%) m.p. 159-160°C (decomp) (ν_{CO} 1952 cm^{-1}; ν_{CO} (acetone) 1710 cm^{-1} [nujol] Found: C, 59.0; H, 4.4; Br, 10.0; Cl, 4.6. Calc. for $C_{76}H_{66}Br_6Cl_2O_2P_4Ru_2$: C, 58.2; H, 4.2; Br, 10.2; Cl, 4.5%) Far i.r. spectrum: 317s, 304m, 280s, 270brs, 260m, 250w, 244w, 236m, 228m, 180brw. ^{31}P nmr (see figure 25).

Di-μ-bromo-μ-chloro-[chlorobis(triphenylphosphine)ruthenium(II)][carbonyl-bis(triphenylphosphine)ruthenium(II)]- acetone (1/1) was prepared as above using [$RuCl_2(PPh_3)_3$] (0.11 g) and [$RuBr_2CO(PPh_3)_3$ dmf] (0.10 g) to give deep red crystals of the product (0.085 g; 51%) m.p. 160-162°C (decomp) (ν_{CO} 1953 cm^{-1}; ν_{CO} (acetone) 1710 cm^{-1} [nujol] (Found: C, 58.5; H, 4.3; Br, 10.0; Cl, 4.6. Calc. for $C_{76}H_{66}Br_2Cl_2O_2P_4Ru_2$: C, 58.2; H, 4.2; Br, 10.2; Cl, 4.5%) Far i.r. spectrum: 317vs, 304w, 280sh, 270brs, 260m, 250w, 244w, 236m, 228m, 180brm. ^{31}P nmr (see figure 25).

Tri-μ-bromo[bromobis(triphenylphosphine)ruthenium(II)][carbonylbis-(triphenylphosphine)ruthenium(II)] acetone (1/1):-

As for the chloro-complex but using $RuBr_2(CO)(PPh_3)_2$dmf (0.1 g) and $RuBr_2(PPh_3)_3$ (0.12 g). Yield 0.13 g (71%) m.p. 154°C (decomp) (ν_{CO} 1952 cm^{-1}; ν_{CO} (acetone) 1710 cm^{-1} [nujol] (Found: C, 55.6; H, 4.2; Br, 19.5. Calc. for $C_{76}H_{66}Br_4O_2P_4Ru_2$: C, 55.1; H, 4.0; Br, 19.3%).

Reaction between $RuCl_2CO(PPh_3)_2$dmf and $RuCl_2(PEtPh_2)_3$:-

$RuCl_2CO(PPh_3)_2$dmf (0.1 g) and $RuCl_2(PEtPh_2)_3$ (0.1 g) were refluxed together in acetone (ca 30 cm^3) under nitrogen for 2½ hours; the red solution was evaporated to small volume and n-pentane added. The bright orange precipitate which formed was filtered and washed with diethylether.

For discussion see page 184

CHAPTER FIVE

REARRANGEMENT REACTIONS OF SOME CARBONYL COMPLEXES OF RUTHENIUM(II) CONTAINING ETHYLDIPHENYLPHOSPHINE LIGANDS

5.1 Introduction

In chapters 3 and 4 the synthesis and rearrangement reactions of triphenylphosphine complexes of ruthenium(II) containing CS_2, CS and CO ligands have been discussed. In order to test the general applicability of the preparative schemes discussed in these preceeding chapters, preliminary investigations have been made into the reactions of the complexes $RuCl_2L_{3 \text{ or } 4}$, (L = PMe_2Ph, $PEtPh_2$) (described in chapter 2) with carbon disulphide and carbon monoxide.†

It has been shown that when a concentrated solution of $RuCl_2(PPh_3)_4$ in acetone is treated with CO, yellow crystals of the complex trans- $RuCl_2(CO)_2(PPh_3)_2$ (LXXIV) (ν_{CO} 2005 cm^{-1}) are deposited.(114) On recrystallisation from CH_2Cl_2/CH_3OH solution they are converted to the white cis- complex (LXXIV) (ν_{CO} 2064, 2001 cm^{-1}).

Monomeric, mono- and di-carbonyl complexes of ruthenium(II) containing other monotertiaryphosphines (L = PEt_3, PMe_2Ph, PEt_2Ph, PPr_2Ph, PBu_2Ph) have been prepared previously by treatment of the corresponding triple halide bridged, ionic dimer $[Ru_2Cl_3L_6]Cl$ with carbon monoxide under varying conditions or by direct reaction between tertiary phosphine, $RuCl_3 \cdot 3H_2O$ and CO (for details of reactions see refs. 36, 114, 126, 129) and their isomeric forms determined such that each species may be characterised by its carbonyl stretching frequency (see table 5:1). However, the ruthenium carbonyl complexes of the type $[RuCl_2COL_2]_2$ and $Ru_2Cl_4COL_4$, L = dialkylaryl- or alkyldiarylphosphine are unknown. It was therefore hoped that these latter complexes might be prepared by means of reactions, similar to those

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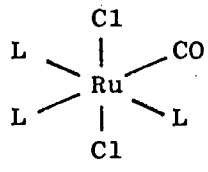
†The reaction of these complexes with carbon disulphide has been the subject of an independent study and is reported elsewhere.(171, 188)

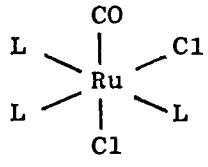
Table 5.1

Isomeric forms and carbonyl stretching frequencies of some mono- and dicarbonyl complexes of ruthenium(II)



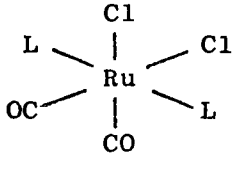
(LXXI)

L	$\nu CO(cm^{-1})$
PMe_2Ph	1961
PEt_2Ph	1960



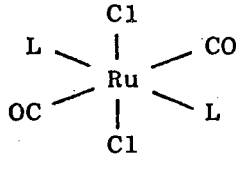
(LXXII)

L	$\nu CO(cm^{-1})$
PEt_3	1916
PMe_2Ph	1943
PEt_2Ph	1942
PPr^n_2Ph	1923
PBu^n_2Ph	1923



(LXXIII)

L	$\nu CO(cm^{-1})$
PEt_3	1968,2037
PMe_2Ph	1972,2037
PEt_2Ph	1980,2037
PPr^n_2Ph	1957,2020
PBu^n_2Ph	1957,2020
PPh_3	2001,2064



(LXXIV)

L	$\nu CO(cm^{-1})$
PEt_3	1984
PMe_2Ph	1996
PEt_2Ph	1999
PPr^n_2Ph	1976
PBu^n_2Ph	1984
PPh_3	2005

All spectra recorded as nujol mulls.

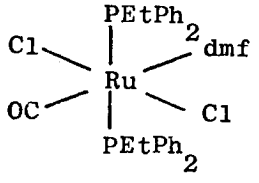
described for the triphenylphosphine complexes, described in chapter 4, starting from the monomers $RuCl_2(PMe_2Ph)_4$ and $RuCl_2(PEtPh_2)_3$.

5.2 Results and Discussion

When the green $RuCl_2(PEtPh_2)_3$ is warmed gently in N,N'-dimethylformamide suspension under a very gentle flow of carbon monoxide, yellow crystals, which analyse well (C,H,N,Cl) for the complex $RuCl_2CO(PEtPh_2)_2$ dmf (LXXV), are deposited.

The infra-red spectrum of this compound shows a single strong band in the carbonyl absorption region at 1928 cm^{-1}. In addition a band at 1641 cm^{-1} shows the presence of a coordinated dmf molecule. The far i.r. spectrum shows that only terminal chloride groups are present (ν Ru-Cl 327 cm^{-1}).

The ^{31}P nmr spectrum of this complex in $CDCl_3$ at 213K shows a singlet at 32.8 ppm which shifts slightly to lower frequency (31.5 ppm) on raising the temperature to 308K. These data support the formulation of the yellow complex as $RuCl_2CO(PEtPh_2)_2$dmf (LXXV) with a structure analogous to the triphenylphosphine complex (LXI).



(LXXV)

Like the corresponding PPh_3 complex, the molecule of solvation in $RuCl_2CO(PEtPh_2)_2$dmf (LXXV) may be exchanged for that of another co-ordinating solvent molecule such as methanol. However, it would appear that in the $PEtPh_2$ complex the dimethylformamide group is more strongly complexed than in the corresponding PPh_3 compound and mixtures

of the two solvated species are obtained. Thus, recrystallisation of (LXXV) from CH_3OH or CH_2Cl_2/CH_3OH produced a mixture of $RuCl_2CO(PEtPh_2)_2$ dmf and $RuCl_2CO(PEtPh_2)_2$ MeOH(ν_{OH}(MeOH) 3550 cm^{-1}; ν_{CO} 1950 cm^{-1}).

In less polar solvents such as dichloromethane (LXXV) behaves in a similar manner to that described earlier for $RuCl_2CO(PPh_3)_2$dmf (LXI)(scheme 4:2). The rate at which these rearrangements occur is much slower for the ethyldiphenylphosphine complex (days as compared to hours for PPh_3). It did not prove possible however, to isolate the rearrangement products in a pure form, nor did it prove possible to obtain satisfactory separations by means of chromatography. As a result elemental analyses were of little use in the characterisation of these complexes. Identification of the products has therefor been made by means of infra-red (carbonyl stretching frequencies) and ^{31}P nmr spectroscopy.

When $RuCl_2CO(PEtPh_2)_2$dmf (LXXV) is shaken in CH_2Cl_2 for 24 hours and the solvent removed by rotary evaporation, a yellow solid (ν_{CO} 2040w., 1970s.br., 1928m. cm^{-1}) is obtained. The ^{31}P nmr spectrum of this mixture at 213K in $CDCl_3$ solution shows a strong singlet at 32.6 ppm. ($RuCl_2CO(PEtPh_2)_2$ dmf); in addition, there is a weak doublet centred at 18.7 ppm, a weak broad resonance at ca 35 ppm, an AB pattern centred at 41.2 ppm (J_{AB} 26.6Hz; δ_{AB} 70Hz) superimposed on some weak resonances and another broad resonance at ca 54.5 ppm (fig 27).

On raising the temperature to 303K the position of the singlet due to (LXXV) moves, as observed previously, to lower frequency. The broad resonance at 35 ppm has sharpened into a triplet (Jpp 25.7Hz) and the doublet at 18.7 ppm (Jpp 25.5Hz) also sharpens. The AB quartet is more intense as are the additional peaks superimposed upon it

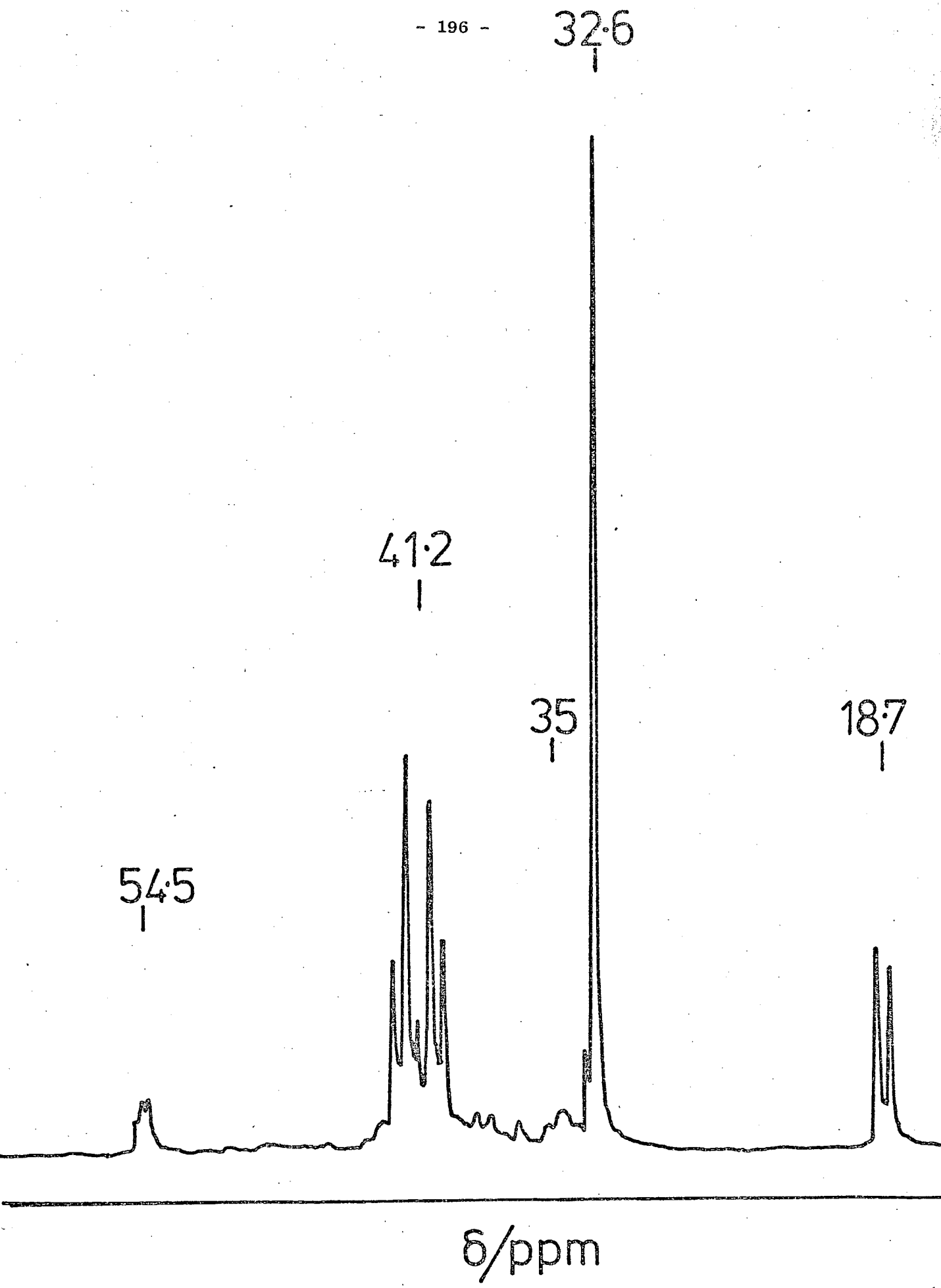


Figure 27 ^{31}P nmr spectrum in $CDCl_3$ at ca 213K of the product obtained on shaking $RuCl_2CO(PEtPh_2)_2$dmf in CH_2Cl_2.

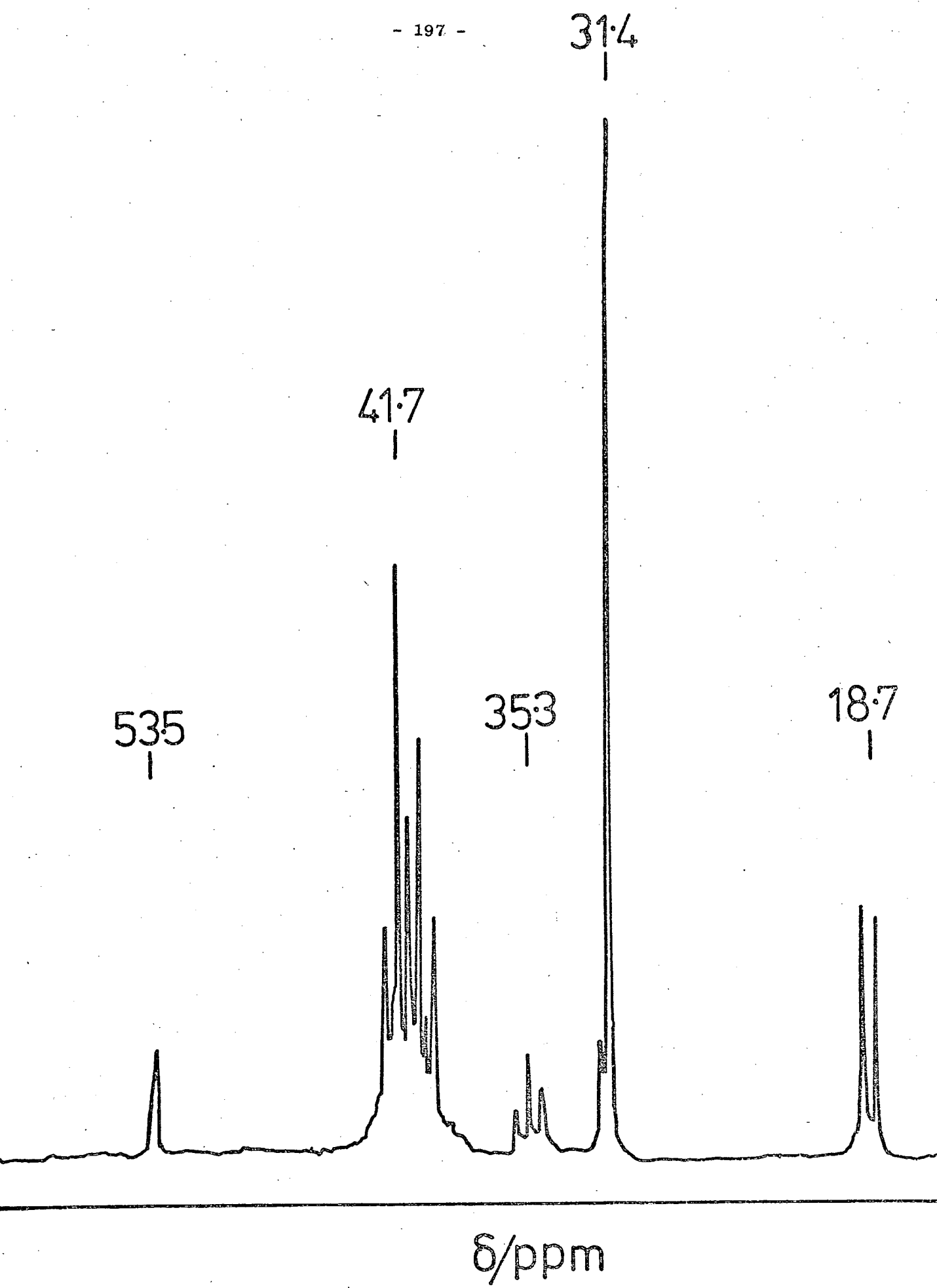


Figure 28 ^{31}P nmr spectrum in $CDCl_3$ at ca 308K of the product obtained on shaking $RuCl_2CO(PEtPh_2)_2$dmf in CH_2Cl_2.

(ca 37 to 44 ppm) and the resonance at 53.5 ppm is now a sharp singlet (fig 28).

When $RuCl_2CO(PEtPh_2)_2$dmf is shaken in benzene for ca 24 hours and the solvent then removed, the infra-red spectrum of the yellow product obtained shows a broad band in the carbonyl stretching region at 1950 cm^{-1}.

The ^{31}P nmr spectrum in $CDCl_3$ at 213K shows no evidence for the AB pattern observed in the spectrum of the product obtained from reaction in dichloromethane. However, the resonances at ca 37 to 44 ppm have increased in intensity and the previously weak resonance at 53.5 ppm now exhibits 3 singlets 55.2, 54.9 and 54.7 ppm. The doublet at 18.9 ppm is also more intense as is the broadened triplet at ca 34 ppm. Unreacted monomer (LXXV) also remains at 32.9 ppm and other weak signals are observed at ca 32, 26 and 20 ppm (fig 29).

On raising the temperature to 303K the resonances in the region 37 to 44 ppm sharpen and move together and a strong singlet is observed at 41.8 ppm. The triplet sharpens and moves to higher frequency (35.3 ppm) (see fig 30).

These observations, with the exceptions of the doublet and triplet patterns, may be interpreted in terms of the scheme 4:2. Thus, by analogy with the triphenylphosphine system it is probable that the weak singlets at ca 32, 26 and 20 ppm correspond to isomers of the double halide bridged complex $[RuCl_2CO(PEtPh_2)_2]_2$ (LXXVI) formed by dimerisation of "$RuCl_2CO(PEtPh_2)_2$". As with $RuCl_2CO(PPh_3)_2$ dmf very little of the double halide bridged species appear to form.

The resonances at 37 to 44 ppm together with the signals at ca 54 ppm (in fig 29) may be assigned as the three isomers of the triple halide bridged dimer $Ru_2Cl_4(CO)_2(PEtPh_2)_3$ (LXXVII)(analogous to (LXII) see table 4:1) which are formed from "$RuCl_2CO(PEtPh_2)_2$" with

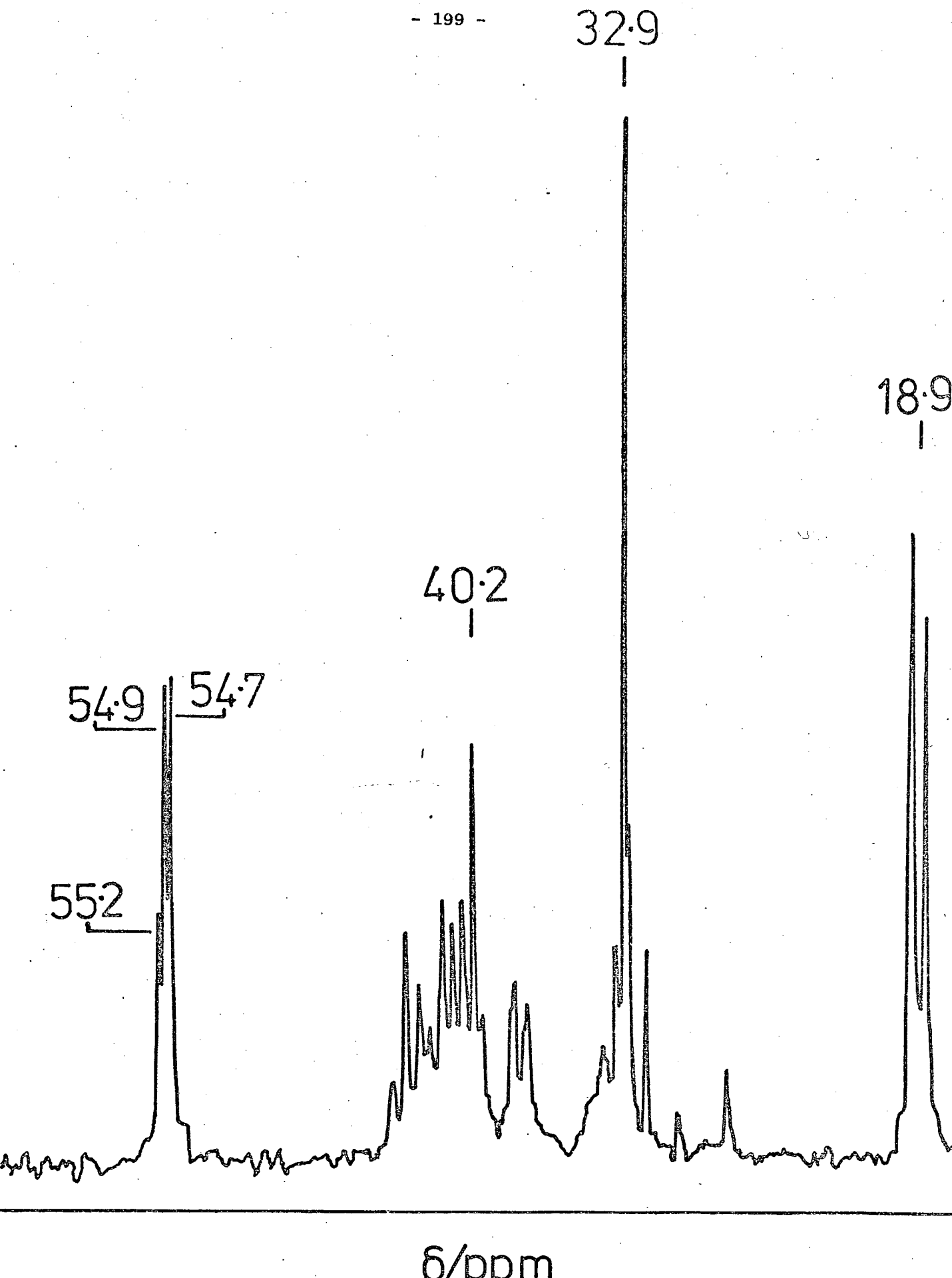


Figure 29 ^{31}P nmr spectrum in $CDCl_3$ at ca 213K of the product obtained on shaking $RuCl_2CO(PEtPh_2)_2$dmf in benzene.

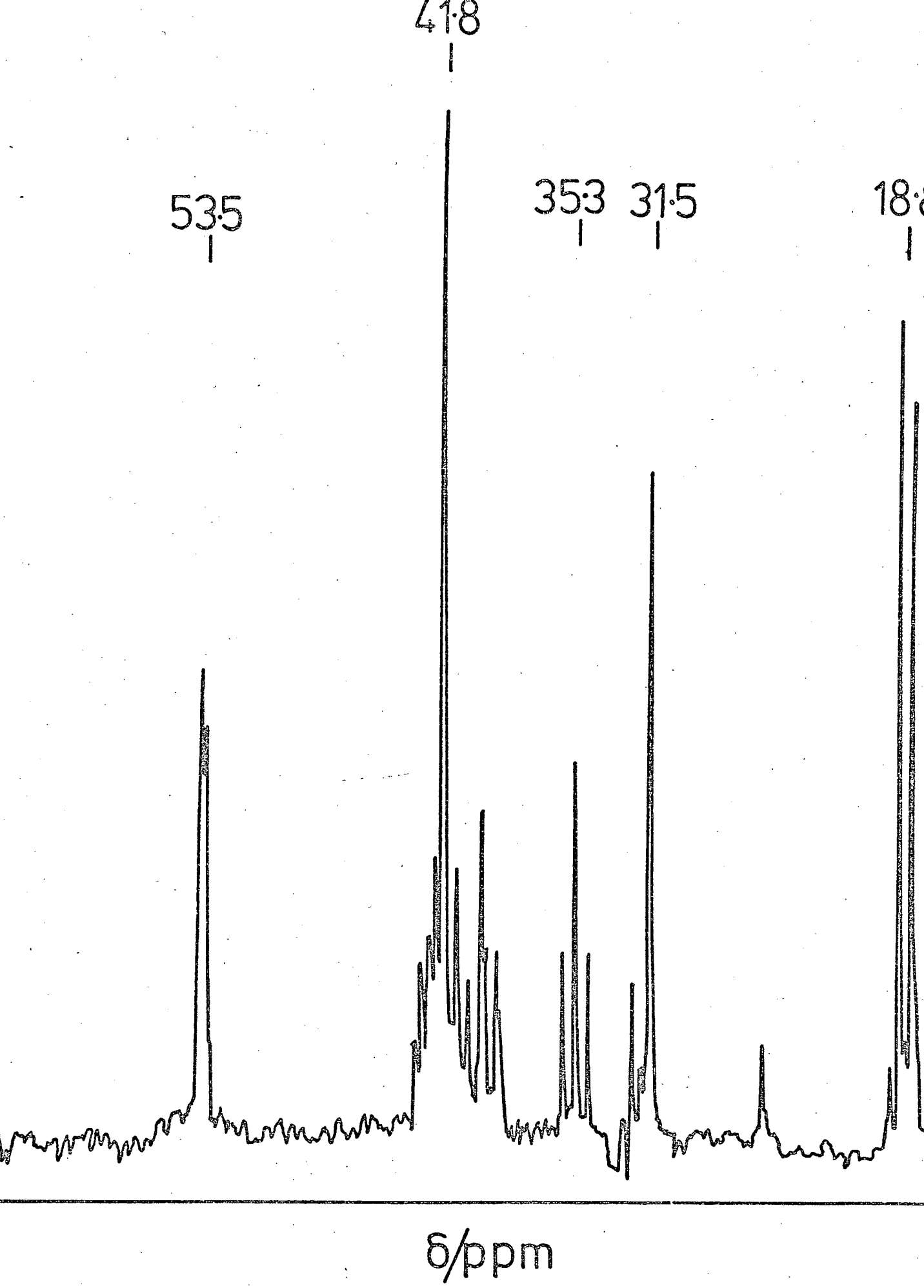


Figure 30 ^{31}P nmr spectrum in $CDCl_3$ at ca 303K of the product obtained on shaking $RuCl_2CO(PEtPh_2)_2dmf$ in benzene.

loss of a $PEtPh_2$ ligand (analogous to step (iv)). On raising the temperature, the resonances sharpen and move closer together and a strong singlet appears at 41.8 ppm. This is probably due either to some form of bridge opening (reverse of step (iv)) or more likely exchange between free and bound phosphine. The complex (LXXVII) is the major product on reaction in benzene.

The AB quartet observed in the ^{31}P nmr spectrum of the dichloromethane reaction, may, again by analogy with the triphenylphosphine system, be assigned to the ionic species $[Ru_2Cl_3(CO)_2(PEtPh_2)_4]Cl$ (LXXVIII). This ionic species did not form (to any significant extent) in solvents less polar than acetone for the PPh_3 complex. That (LXXVIII) should form in CH_2Cl_2 solution for the $PEtPh_2$ system indicates the greater affinity of $PEtPh_2$ for ruthenium(II) (as chloride is displaced in preference to phosphine).

In addition, as a mixture of the species $RuCl_2CO(PEtPh_2)_2dmf$, $[RuCl_2CO(PEtPh_2)_2]_2$ and $Ru_2Cl_4(CO)_2(PEtPh_2)_3$ is obtained, even after reaction for 24 hours in benzene it appears in this instance (unlike the PPh_3 complexes) that either the steps (ii) (iii) and (iv) (scheme 4:2) are slow, or that the equilibria for these reactions lie further to the left. This again shows the greater lability of Ru-PPh_3 bonds compared with those of the other tertiary-phosphines.

During the formation of $Ru_2Cl_4(CO)_2L_3$ from "$RuCl_2COL_2$" free tertiary phosphine is liberated. In the case of triphenylphosphine this is observed in the ^{31}P nmr spectrum as free PPh_3 (-6 ppm) or as triphenylphosphineoxide ($OPPh_3$, 29 ppm). However in the reaction with $RuCl_2CO(PEtPh_2)_2dmf$ no free $PEtPh_2$ (-15.5 ppm) or $OPEtPh_2$ (35 ppm)[10] is observed. In addition a doublet and triplet pattern (18.9 and 35.3 ppm; Jpp 25.7 Hz),

which are not present in the spectrum of the PPh_3 complexes, are seen to grow in intensity with increasing reaction time. These resonances may be attributed to the monocarbonyl complex $RuCl_2CO(PEtPh_2)_3$ (structure (LXXII)).†

This complex could be formed either by displacement of dmf from (LXXV) or by direct reaction of $PEtPh_2$ with the five co-ordinate intermediate species. No evidence for $RuCl_2CO(PPh_3)_3$ was observed in the triphenylphosphine system probably because $RuCl_2CO(PPh_3)_3$, due to the greater steric size of PPh_3, is unstable with respect to "$RuCl_2CO(PPh_3)_2$" and PPh_3.

An attempt to prepare the triple halide bridged complex $Ru_2Cl_4CO(PEtPh_2)_4$ by a "coupling reaction" between $RuCl_2CO(PEtPh_2)_2$ dmf and $RuCl_2(PEtPh_2)_3$ in acetone (see scheme 4:2 step (vii)) produced a bright orange material (ν_{CO} 1960 br).

The ^{31}P nmr spectrum of this material at 213K consisted of a strong doublet resonance at 18.9 ppm, 3 broad resonances at 49.0, 34.1 and 31 ppm, two AB resonances centred at 48.5 ppm (J_{AB} 40.1Hz; δ_{AB} 191.3Hz) and 39.4 ppm (J_{AB} 26.2Hz; δ_{AB} 139.5Hz) and a weak singlet at 36.8 ppm (possibly due to some $RuCl_2CO(PEtPh_2)_2$acetone) (see fig 31).

At 303K the latter disappears and the broad resonance at ca 34 ppm sharpens to a triplet at 35.3 ppm (Jpp 25.5Hz) which together

---

†Attempts to prepare a genuine sample of this complex by recrystallisation of $RuCl_2CO(PEtPh_2)_3$ isomer (LXXI)(prepared by treating the "red solution" with $PEtPh_2$) from 2-methoxyethanol[36] gave the ionic complex (LXXVIII). The structure (LXXII) is attributed to $RuCl_2CO(PEtPh_2)_3$ formed above by analogy with the relative positions of the doublet and triplet in $RuCl_2CO(PMe_2Ph)_3$ isomer (LXXII) viz- -1.2 ppm and 18.0 ppm respectively.

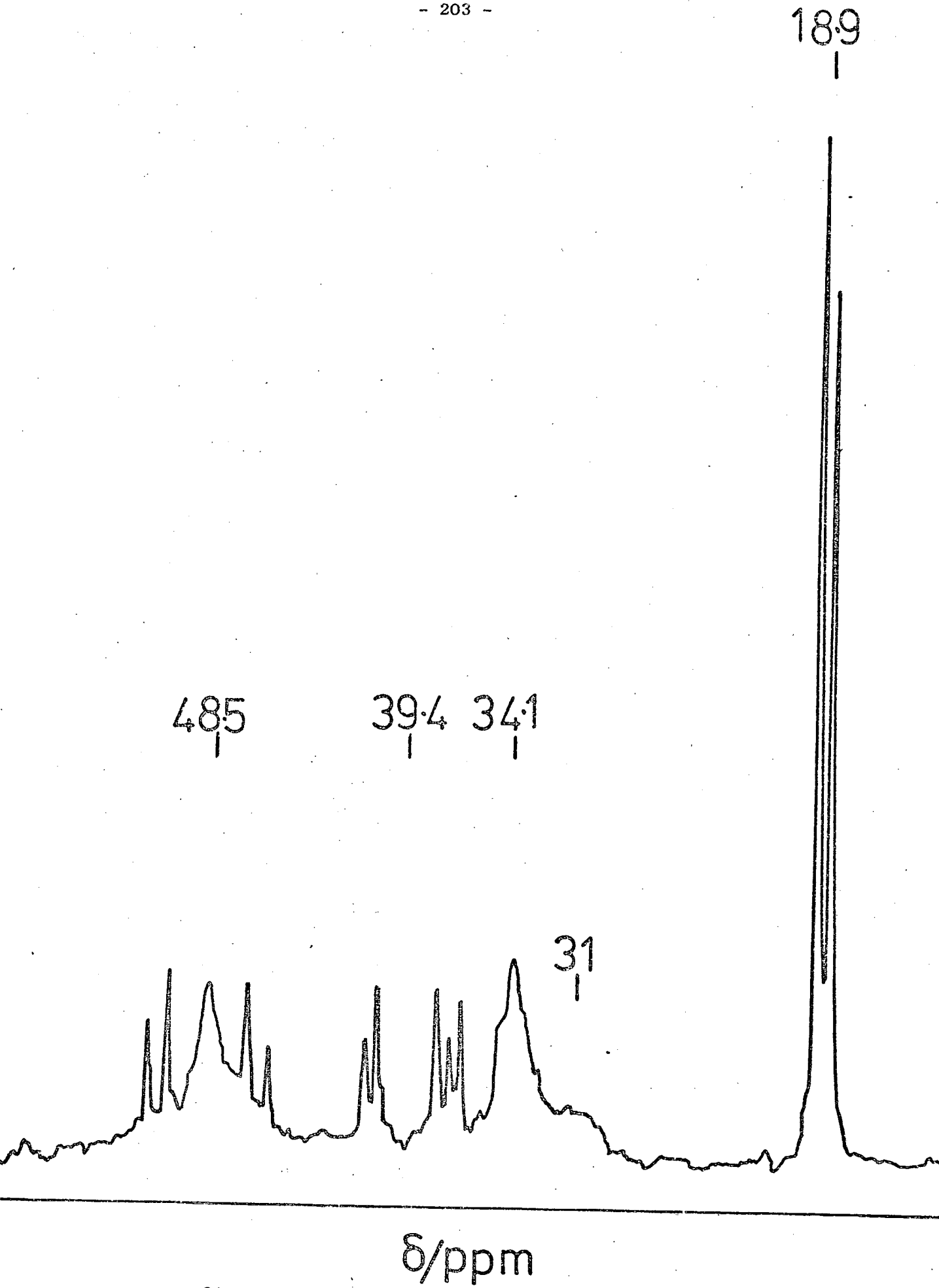


Figure 31 ^{31}P nmr spectrum in $CDCl_3$ at ca 213K of the product obtained by reaction of $RuCl_2(PEtPh_2)_3$ with $RuCl_2CO(PEtPh_2)_2$dmf in acetone.

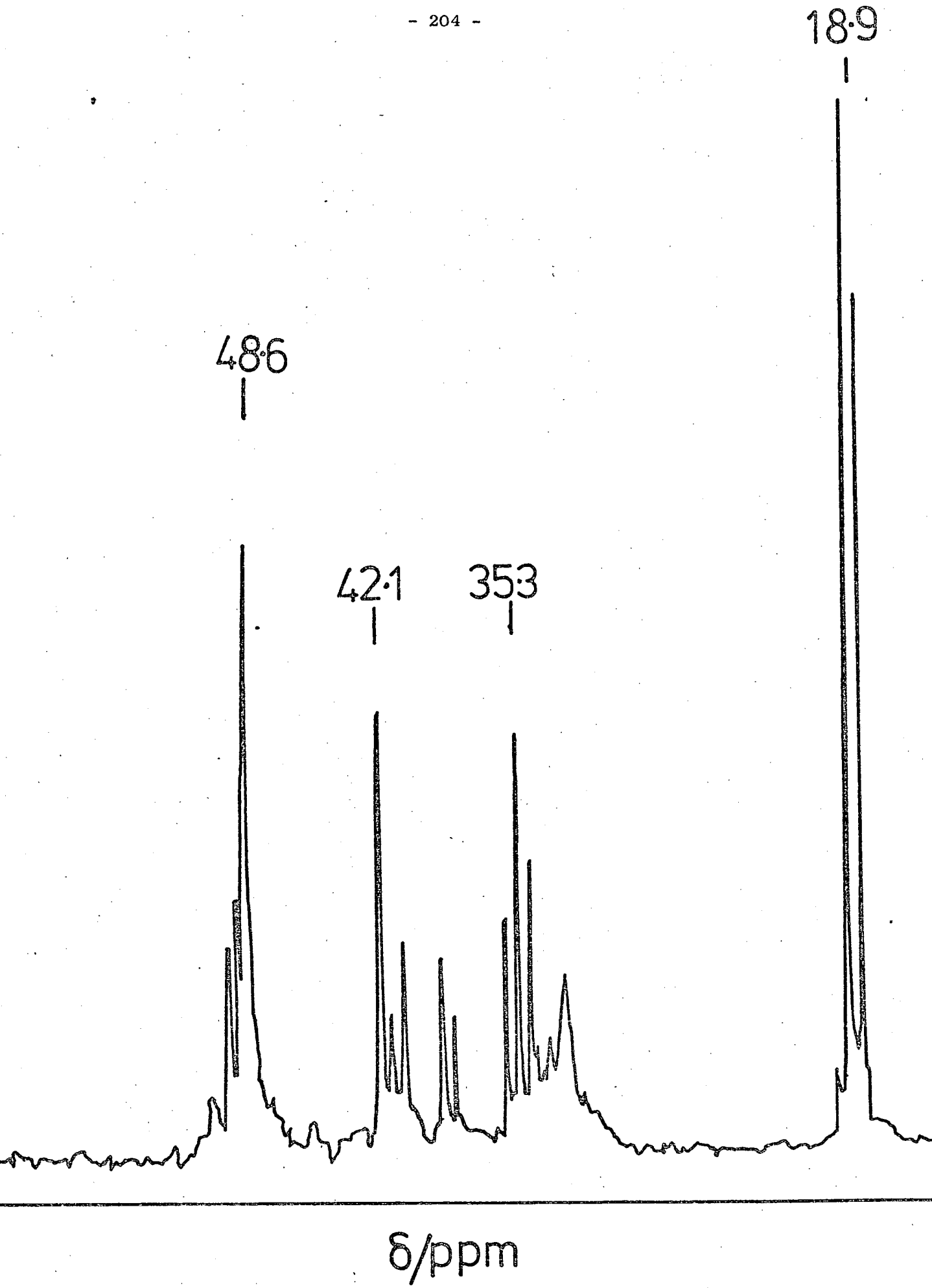
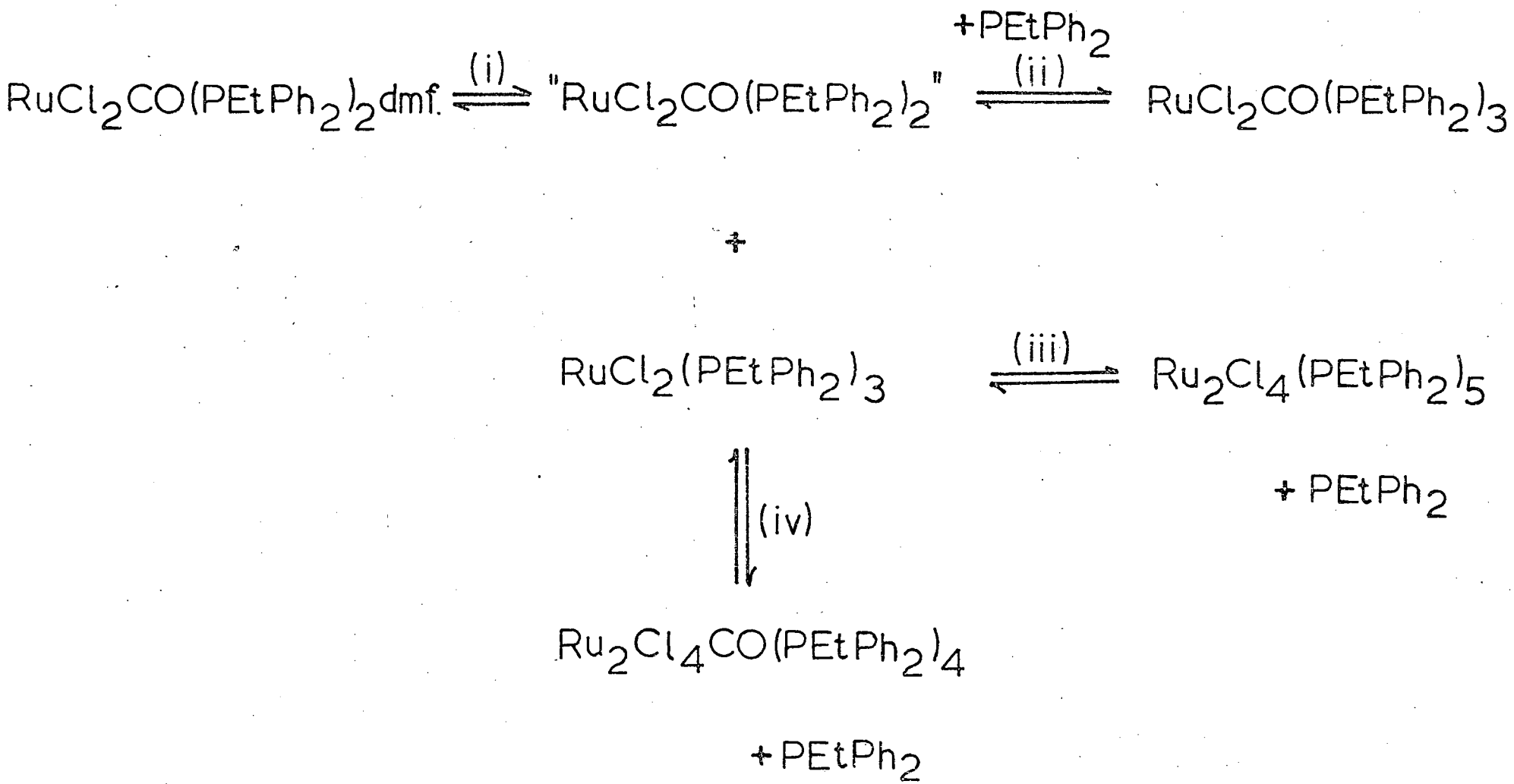


Figure 32 ^{31}P nmr spectrum in $CDCl_3$ at ca 303K of the product obtained by the reaction of $RuCl_2(PEtPh_2)_3$ with $RuCl_2CO(PEtPh_2)_2$dmf in acetone.


RuCl2CO(PEtPh2)2dmf.
(i)
"RuCl2CO(PEtPh2)2"
+PEtPh2
(ii)
RuCl2CO(PEtPh2)3
+
RuCl2(PEtPh2)3
(iii)
Ru2Cl4(PEtPh2)5
+ PEtPh2
(iv)
Ru2Cl4CO(PEtPh2)4
+PEtPh2

Scheme 5·1

that the dicarbonyl complex forms in preference to the dmf species. Finally, attempts to prepare $Ru_2Cl_4CO(PEt_2Ph)_4$ by replacing a PEt_2Ph ligand in $Ru_2Cl_4(PEt_2Ph)_5$ with CO indicated that bridge opening or bridge cleavage were probably occurring in preference to phosphine displacement.

5.3 Conclusions

The behaviour of the complex $RuCl_2CO(PEtPh_2)_2$ dmf in solution is similar to that of the corresponding PPh_3 complex (LXI). However, as expected, the ethyldiphenylphosphine ligand proved less labile than the triphenylphosphine. Both this and the tendency of $RuCl_2(PEtPh_2)_3$ to dimerise to $Ru_2Cl_4(PEtPh_2)_5$ led to mixtures of products.

The reactions of $RuCl_2L_4$ (L = PMe_2Ph, $PMePh_2$) and $Ru_2Cl_4(PEt_2Ph)_5$ with carbon monoxide in both coordinating and non-coordinating solvents, require a full and detailed study. Also, the "coupling reactions" described in chapters 4 and 5 using $RuCl_2COL_2$dmf (L = PPh_3, $PEtPh_2$) should be investigated further with a view to providing a possible route to the synthesis of mixed phosphine complexes and also halide bridged complexes containing more than one type of transition metal.

5.4 Experimental

Physical measurements were performed as described in chapter 2.

Dichlorocarbonyl N,N^1-dimethylformamide bis(ethyldiphenylphosphine) ruthenium(II):

$RuCl_2(PEtPh_2)_3$ (0.15g) was suspended in N,N^1-dimethylformamide (1.5 cm^3) and warmed gently in a very slow stream of carbon monoxide. Yellow crystals of the product were deposited. The suspension was cooled in ice when all of the green starting material had reacted (ca 5-10 mins) and diethyl ether was added. The complex was filtered and well washed with diethyl ether and pentane and dried in vacuo at 313K (0.76g: 60%) (M.P. 167°decomp)[Found C, 54.6; H, 5.3; N, 2.1; Cl, 10.2%: Calculated for $C_{32}H_{37}NO_2P_2Cl_2Ru$: C, 54.8; H, 5.3; N, 2.0; Cl, 10.1%]

Reaction of $RuCl_2CO(PEtPh_2)_2$dmf in dichloromethane solution:

$RuCl_2CO(PEtPh_2)_2$dmf was shaken in dichloromethane solution under nitrogen for 10 hours. Light petroleum (bp 60-80°) was added to the resulting yellow solution and most of the solvent removed when a pale yellow powder precipitated. The solid was filtered and washed with diethyl ether. For discussion of the ^{31}P nmr and I.R. spectra of this solid see page 195

Reaction of $RuCl_2CO(PEtPh_2)_2$dmf in benzene solution:

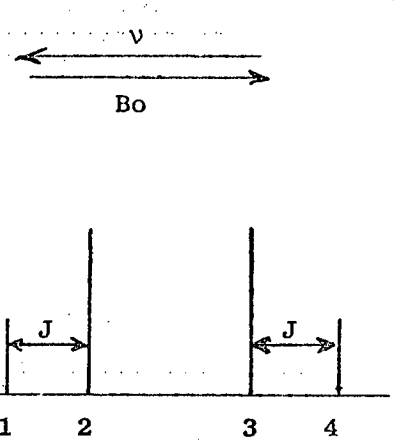
$RuCl_2CO(PEtPh_2)_2$dmf was shaken in benzene under nitrogen for 24 hours. The solvent was then removed by rotary evaporation to give an orange oil which was dissolved in dichloromethane (ca 2 cm^3). Light petroleum (bp 60-80°) was added slowly to give a yellow-orange solid which was filtered and washed with pentane. For discussion of the ^{31}P nmr and I.R. spectra of this solid see page 198

Reaction of $RuCl_2CO(PEtPh_2)_2dmf$ with $RuCl_2(PEtPh_2)_3$:

$RuCl_2CO(PEtPh_2)_2dmf$ (0.07g) and $RuCl_2(PEtPh_2)_3$ (0.08g) (1:1 molar ratios) were refluxed in acetone (ca 30 cm^3) under nitrogen for 5 hours. The solution was cooled and evaporated to ca 5 cm^3. An excess of light petroleum (bp 60.80°) was added and the resulting orange solid filtered. For discussion of the ^{31}P nmr and I.R. spectra of this solid see page 202

Appendix I

Analysis of an AB type nmr spectrum.



Coupling constant

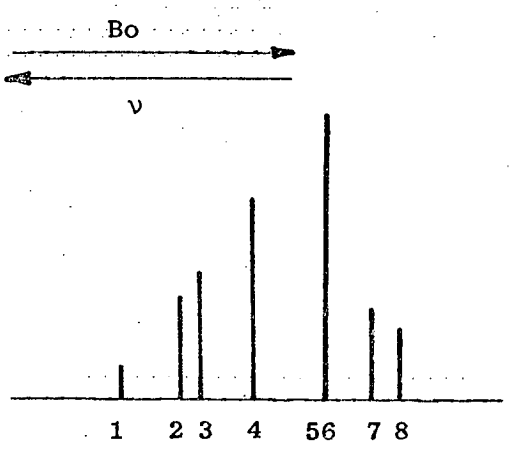
$$J = \nu_1 - \nu_2 = \nu_3 - \nu_4$$

Chemical shift difference between nuclei A and B.

$$\Delta\nu = [\,(\nu_1 - \nu_4)(\nu_2 - \nu_3)\,]^{\frac{1}{2}}$$

Appendix II

Analysis of an AB_2 type nmr spectrum.



The chemical shift of nucleus A, ν_A, is given by line 3.

The chemical shift of nucleus B, ν_B, is given by the mean of lines 5 and 7.

The coupling constant J_{AB} is given by

$$J_{AB} = {}^1/_3[(\nu_8 - \nu_6) + (\nu_4 - \nu_1)]$$

In many spectra it is difficult to resolve lines 5 and 6 this may lead to uncertainty in the values of J_{AB} and ν_B.

When the value of $J_{AB}/\Delta\nu > 1$ line 1 becomes very weak.

If either of the above should occur then the spectrum may be analysed by:-

Either (A) Fitting the observed spectrum to a plot of the calculated positions such as may be found in Appendix D section 1 of Ref. 8

or (B) using the value of ν_A and the approximate value for ν_B compile a table of values for $\frac{\nu_n - \nu_A}{\nu_A - \nu_B}$

ν_n is the frequency of lines 1 to 8

Then by fitting the values obtained to the graph on page 70 of Ref (2) an approximate value for $J/_{\Delta\nu}$ can be found.

when a more precise analysis can then be obtained by computer simulation or by comparison of the observed spectrum with the values for line positions and intensities tabulated in Appendix D of Ref. (7).

APPENDIX III

ABBREVIATIONS

acac	-	acetylacetonate
bipy	-	2,2' - bipyridyl
COD	-	1,3- or 1,5- cyclooctadiene
Cp	-	cyclopentadiene
diars	-	o-phenylenebis(dimethylarsine)
diphos	-	ethylenebis(diphenylphosphine)
dmf	-	NN-dimethylformamide
mes	-	mesityl
OT	-	ortho-tolyl
phen	-	1,10-phenanthroline
py	-	pyridine

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Post Graduate Courses Attended

" ^{13}C and Fourier Transform N.M.R."	by Dr. D. Shaw.
"Crystal Structure Determination"	by Dr. R.O. Gould Dr. M.M. Harding Dr. D.W. Green
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